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Modified Rotationally Adiabatic Model for Rotational Autoionization  
of Dipole-Bound Molecular Anions

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Abstract

Modifications are introduced to a rotationally adiabatic model developed and successfully applied by Clary to describe rotational autoionization of dipole-bound molecular anions. These modifications address branching ratios for forming neutrals in various final rotational states. They also produce rate-enhancement corrections to the original model in the neighborhoods of channel openings. Example calculations are presented and the essential ingredients of the corrections are tabulated in a manner that permits straightforward application to any linear or pseudo-linear (i.e., symmetric top with  $\Delta K=0$ ) anion.

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## I. Introduction

A computationally tractable and physically clear model for rotational autoionization of dipole-bound states of molecular anions has recently been put forth<sup>1a</sup> by Clary. In this model, the "extra" electron, originally bound and locked to a molecule-fixed axis system, gains energy from the molecule's rotational degrees of freedom and is eventually ejected, leaving the molecule with less rotational energy. The energy levels of the anion relative to those of the neutral molecule and the autoionization lifetimes of these levels are predicted within Clary's model in terms of the dipole moment and rotational constants of the neutral molecule. Although this model has been remarkably successful<sup>1a</sup> in interpreting trends in the experimental spectra<sup>1b</sup> of these metastable states, certain aspects of the data require enhancement of the original model. It is in this spirit that the developments presented here are put forth.

## II. Overview of Clary's Original Rotationally Adiabatic Model

### A. The Angular Basis Functions and the Rotationally Adiabatic Curves

To introduce the main concepts and notation of the rotationally adiabatic (RA) model<sup>1a</sup>, it is adequate to consider an electron bound to a rotating diatomic species<sup>2</sup> whose vibrationally averaged rotational constant is denoted  $b_v$ . To describe states of a given total angular momentum  $J$  and projection  $M$  along the lab-fixed  $z$ -axis, the following basis of angular functions is formed

$$|J, M; j, l\rangle = \sum_m \langle j, m, l, M-m | J, M \rangle |j, m\rangle |l, M-m\rangle.$$

These functions consist of coupled products of molecular rotor ( $|j, m\rangle$ ) and electronic ( $|l, M-m\rangle$ ) angular functions. A model Hamiltonian containing a molecular rotor part ( $b_v j^2$ ), an electron-molecule potential  $V$ , and an electronic angular-plus-radial kinetic energy part is also introduced

$$H = b_v j^2 + V + l^2 / 2m_e R^2 + \hbar^2 / 2m_e 1/R^2 (\partial/\partial R (R^2 \partial/\partial R)).$$

The electron-molecule potential is taken, for these dipole-bound anion states, to be of the form

$$V(R, \theta) = \mu \cos(\theta) / R^2 F(R),$$

where  $F(R)$  includes the effect of the electron-polarizability interaction and a "cut off" function designed to smoothly remove the singularity in the potential as  $R$  approaches zero.

The key construct of the original RA model as put forth by Clary is the set of so-called rotationally adiabatic potential curves generated by diagonalizing, within the angular basis described above, the Hamiltonian in the absence of electronic radial motion

$$H^0 = b_v j^2 + V + l^2 / 2m_e$$

for fixed electron-molecule distance  $R$ . For each fixed  $J$  value, Clary found that the lowest rotationally adiabatic potential curve generated in this manner was attractive at small  $R$ , had a "barrier" at intermediate  $R$  values, and approached the energy of the  $j = 0$  rotor at large  $R$ . The physical origins of these attributes of this lowest potential are discussed below in Sec. III.

#### B. The Dipole-Bound State Energies and Lifetimes

The RA model evaluates the dipole-bound anion's electronic energies and autoionization lifetimes by using the lowest RA potential curve (call it  $E_0(R)$ ) to solve for the radial motion of the electron. The energies of the resultant quasi-stationary states and their lifetimes (which are governed by the rate of tunneling through the barrier in  $E_0(R)$ ) are obtained from this radial Schrödinger equation's solution. Much of the solution was carried through analytically<sup>1a</sup> by Clary, and many of the trends in decay rates as functions of rotational quantum numbers, dipole moment, and isotopic substitution were beautifully explained by this model.

### III. Observations Leading to Modification of the Clary Model

#### A. The Nature of Rotationally Adiabatic Energies

It is important to understand the physical nature of the lowest rotationally adiabatic potential  $E_0(R)$  and of the corresponding angular eigenfunction  $\Phi_0(R)$  formed as a linear combination of the above  $|J,M; j,l\rangle$  basis states with coefficients that depend on  $R$ :

$$\Phi_0(R) = \sum_{j,l} C_{0,j,l}(R) |J,M; j,l\rangle .$$

This angular function, multiplied by the solution ( $F(R)$ ) of the radial Schrödinger equation, forms the full electronic-rotational wavefunction within this model:  $\Psi = \Phi_0 F(R)$ . To understand the nature of the couplings among the  $|J,M; j,l\rangle$  that give rise to  $E_0(R)$  and  $\Phi_0(R)$ , consider the "diabatic energies" given by the expectation values of  $H^0$  for each of the angular basis states  $|J,M; j,l\rangle$ :

$$E_{j,l}^0(R) = \langle J,M; j,l | H^0 | J,M; j,l \rangle = b_v j(j+1) + l(l+1) \hbar^2 / 2m_e R^2 .$$

Because the angular dependence of  $V$  is of the form  $\cos(\theta)$ , the average value of  $V$  taken over any single  $|J,M; j,l\rangle$  function vanishes. Thus, in the absence of couplings among the angular basis states, one has a picture of diabatic potentials  $E_{j,l}^0(R)$  which undergo multiple crossings as depicted below in Fig. 1.

Couplings among angular basis states which have the same  $J$  and  $M$  values ( these two quantum numbers are conserved by the full Hamiltonian  $H$ ) but which differ by unity in their  $j$  (and hence  $l$ ) quantum numbers can be realized through the angular dependence of  $V(R,\theta)$ . At small  $R$ , where  $E_{J,0}^0$  and  $E_{J-1,1}^0$  undergo a crossing, the

two basis states with  $j=J, l=0$  and  $j=J-1, l=1$  mix to form a hybrid state  $\Phi_0$  (i.e., they combine to dominate the sum  $\sum_{j,l} C_{0,j,l}(R) |J,M; j,l\rangle$  at such values of  $R$ ) whose average interaction with the electron  $\langle \Phi_0 | V | \Phi_0 \rangle$  is non-zero. This hybrid state consists of an electron in an  $l=0, l=1$  hybrid orbital<sup>3</sup> bound and locked to the diatomic molecule's axis with the molecule rotating in a manner to produce total angular momentum  $J$ . Binding is caused largely by attraction of the electron to the positive end of the molecule's dipole field.

At larger values of  $R$ ,  $E_{J-1,1}^0$  and  $E_{J-2,2}^0$  undergo a crossing; here  $\Phi_0$  picks up a strong component of  $j=J-2, l=2$  character, and  $E_0(R)$  evolves to track  $E_{J-2,2}^0(R)$  beyond this crossing until the next crossing is reached. Subsequent crossings between  $E_{J-n,n}^0$  and  $E_{J-n-1,n+1}^0$  occur at  $R_{J-n,J-n-1} = \{ (n+1) / (2b(J-n)) \}^{1/2}$  at energies of  $E_{J-n,J-n-1} = b(J-n)(J+1)$ . These crossing energies lie above the neutral's rotational state  $J-n$  (whose energy is  $b(J-n)(J-n+1)$ ) by an amount<sup>4</sup>  $nb(J-n)$ . As subsequent crossings are reached, couplings between the  $j=J-n, l=n$  component of  $\Phi_0$ , which exists as dominant from the preceding crossing, and the  $j=J-n-1, l=n+1$  component give rise to a new ( $j=J-n-1, l=n+1$ ) contribution to  $\Phi_0$  and to a further lowering of  $E_0(R)$  as this potential moves from tracking  $E_{J-n,n}^0$  to track  $E_{J-n-1,n+1}^0$ .

#### B. Problem with Using $E_0(R)$ at Large $R$

One difficulty of the original rotationally adiabatic model should now be clear; by forming  $E_0(R)$  in this manner and solving for the radial motion of the electron on the single potential surface  $E_0(R)$ , one restricts the autoionization process to yield a state  $\Psi = \Phi_0 F(R)$  which contains only  $j=0, l=J$  components at large  $R$  because,  $\Phi_0$  contains, at any  $R$ , primarily that  $j,l$  component arising from the last crossing encountered. This model does not allow for the formation of the numerous final states (e.g.,  $j=J-1, J-2, \dots, 3, 2, 1, 0$  may be energetically accessible) that may be "open" (i.e., accessible). To extend the model in a manner that will allow final-state branching ratios to be addressed requires treatment of the multi-channel nature of the electron-ejection dynamics.

It is natural to wonder how this model was able to provide so much insight into the energy level patterns and (total) decay lifetimes of the dipole-bound states which it is designed to mimic. The answer lies in the observation that the positions (i.e., energies) and lifetimes of the states obtained by solving the radial Schrödinger equation on  $E_0(R)$  depend primarily on the form of  $E_0(R)$  where this potential is attractive (for the positions) and on the height and width of the barrier at these energies (for the lifetimes). Beyond the barrier,

where the electron no longer is bound, is it unreasonable to make the rotationally adiabatic approximation. Thus, the form of and use of  $E_0(R)$  is correct at those  $R$  values (i.e., small  $R$  and throughout most of the barrier region) that affect the positions and lifetimes of the states. The fact that Clary's rotationally adiabatic  $E_0(R)$  does not provide an adequate description of the dynamics beyond the barrier, where a multi-open-channel picture is needed and where the electron is no longer locked to the molecular axis, has very little influence on the model's predicted energies and total (not branching-specific) lifetimes.

### C. The Predicted Rotational Energy Level Patterns

In addition to the need to augment the original Clary model by including a multi-open-channel treatment at large  $R$ , the rotational energy level pattern obtained from the original model is not accurate enough to characterize certain aspects of the experimentally observed lifetime trends. In particular, the original model expresses the rotational energies of the dipole-bound states in terms of only one set of rotational constants—those of the daughter neutral molecule. The anion's energies are expressed in terms of these rotational constants and the dipole moment of the neutral molecule. As given explicitly in Eq.(14) of ref.1a, the energy levels of the dipole-bound anion states (e.g.,  $E_{res}(K',J') = -C(b) + bJ'(J'+1) + (a-b)K'^2$ , for a symmetric top case) are related to those of the neutral by a single negative constant  $-C(b)$  which is independent of rotational quantum numbers. This constant shift (i.e., the electron affinity EA) in the anion energies relative to those of the neutral is an integral part of the original model. This gives rise to a situation in which:

1. For an electron affinity EA of the dipole-bound state, the lowest state of the anion which can detach has  $J' (J'+1) b \cong EA$ . This state can detach only via a  $\Delta J \cong J'$  process.
2. As one moves to higher  $J$  values within the dipole-bound anion's rotational "ladder", smaller and smaller  $\Delta J$  processes become open (see the table below).
3. Eventually, for high enough  $J$ , one reaches a situation in which  $\Delta J = 1$  is open, but one never realizes the  $\Delta J = 0$  situation. From these  $J$  values on,  $\Delta J = 1$  remains open.

Such a progression from initially large  $\Delta J$  through smaller  $\Delta J$  values as  $J'$  increases is often seen experimentally; however, there are interesting cases<sup>5</sup> in which the pattern of  $\Delta J$  values is qualitatively different. It turns out that substantial errors in calculated detachment rates can occur when the original model incorrectly predicts the anion-neutral state spacings in regions where

$\Delta J$  is changing. For example, for  $J'$  values where  $\Delta J = 2$  transitions are experimentally seen to be closed but nearly open, the original model may (incorrectly) predict  $\Delta J = 2$  to be open. It is important to correct such small errors in the state energies predicted by the original model in these special cases where  $\Delta J$  is incorrect because these errors may lead to qualitatively incorrect neutral-state branching ratios. As shown below, these same corrections, combined with modification of the model introduced to more properly treat the asymptotic multi-channel issues, allow one to better understand the sudden rises in detachment rate that can accompany new channel openings (i.e., smaller  $\Delta J$  values becoming open).

#### IV. The Modified Rotationally Adiabatic Model

To overcome the lack of multiple-open-channels at large  $R$  and to represent the anion-neutral energy level patterns in a manner which allows progressive channel openings to be consistent with different values for  $b^0$  and  $b^-$ , the original rotationally adiabatic model can be modified as follows:

A. Beyond the crossing point  $R_{J-n, J-n-1} = \{(n+1)/(2b(J-n))\}^{1/2}$  of the first open channel ( $J-n$ ), the full multitude of open-channel surfaces are brought into consideration and the electronic function is permitted to develop amplitudes for each such channel. In the simplest treatment of this aspect of the problem, a Landau-Zener model can be used to estimate the amplitudes of the final-states whose crossing energies  $E_{J-n, J-n-1} = b(J-n)(J+1)$  occur below the dipole-bound state's energy  $E$ . Decay into final states whose crossing energies lie above  $E$  can be treated perturbatively as described below.

B. To more accurately represent the relative orderings of the dipole-bound-anion and neutral-molecule rotational states and thereby achieve a more correct description of the  $\Delta J$  pattern, the energies obtained by solving the radial Schrödinger equation on  $E_0(R)$  are "fine tuned" by simply correcting them to fit the experimentally observed pattern. The necessary corrections are small and should not substantially affect the tunnelling rates calculated within this model because the width of the barrier is only weakly dependent on the position (energy) of the state for such small energy variations. The primary effect of such energy shifting is to close or open channels which the original model (with  $b^0 = b^-$ ) incorrectly identified. These channel-opening corrections can have substantial effects on the calculated detachment rates and branching ratios.



## V. Implementation of the Modified Model

After "fine tuning" the rotational levels of the dipole-bound anion predicted by the original model (labeled by J or J,K for diatomic or symmetric top species, respectively) so as to correctly identify the first energetically available neutral-molecule state (label it  $J_i = J-n$ ) for each anion state J, the total rate of autoionization is first computed as in the original rotationally adiabatic model. Beginning with the state J-n, branching ratios are then calculated. For open channels whose crossing energies lie below the anion's energy E, the Landau-Zener (LZ) method as detailed below is used. For open channels whose crossing energies  $E_{J-n, J-n-1}$  lie above E (such channels are denoted "frustrated"), the perturbative method given below is used. This treatment of the frustrated channels also provides a correction to the overall tunnelling detachment rate predicted by the original model, arising from channel-opening effects.

### A. Perturbative Treatment of Frustrated Channels

For open channels whose crossing energies  $E_{J-n, J-n-1}$  lie above E, one can estimate the branching ratios between the corresponding pairs of states ( $j=J-n, l=n$  and  $j=J-n-n, l=n+$ ) by considering the  $2 \times 2$  couplings between successive pairs of states. As the diabatic surfaces  $E^0_{J-n, n}(R)$  and  $E^0_{J-n-1, n+1}(R)$  couple through  $V_{J-n, J-n-1}(R)$ , the mixing coefficients  $C_{J-n}$  and  $C_{J-n-1}$  corresponding to the two coupled states will vary with R. For the highest energy frustrated state, the wavefunction  $\Phi_0(R)$  brings to the  $R_{J-n, J-n-1}$  crossing a dominant amplitude for the  $j=J-n$  state. To estimate the amplitude of the  $j=J-n-1$  state once this crossing point has been passed, perturbation theory can be used and gives:

$$C_{J-n-1}/C_{J-n} = V_{J-n, J-n-1}(R)/[E - E^0_{J-n-1}(R)].$$

The probability that the system would "hop" from the diabatic state with  $j=J-n$  to that with  $j=J-n-1$  as it passes through this crossing is:

$$P_{n, n+1} = |C_{J-n-1}|^2 / [|C_{J-n-1}|^2 + |C_{J-n}|^2];$$

the probability that it would remain on the state with  $j=J-n$  is  $(1 - P_{n, n+1})$ .

The energy can reasonably be expressed as  $E = b(J-n)(J-n+1) + fnb(J-n)$  since, by assumption, this dipole bound state lies above the  $j=J-n$  state of the neutral and below the crossing which occurs at  $R_{J-n, J-n-1} = \{ (n+1)/(2b(J-n)) \}^{1/2}$  with energy  $E_{J-n, J-n-1} = b(J-n)(J+1)$ . Here f parameterizes the state energy E in terms of the spacing  $(nb(J-n))$  between  $E_{J-n, J-n-1}$  and  $E_{J-n}$ . Just beyond the crossing point, where the wavefunction's flux bifurcates, the square of the amplitude ratio can thus be estimated as:

$$|C_{J-n-1}|^2 / |C_{J-n}|^2 = 4(V_{J-n,J-n-1}^0)^2 / [(1-f)^2(n+1)^2n^2],$$

where the matrix element of  $V$  between the two diabatic states  $V_{J-n,J-n-1}$  has been written in as  $V^0/R^2_{J-n,J-n-1}$ . These estimates for the amplitude ratios lead to the following predictions for the hopping probabilities involving frustrated states:

$$P_{n,n+1} = 4(V_{J-n,J-n-1}^0)^2 / [n^2(n+1)^2(1-f)^2 + 4(V_{J-n,J-n-1}^0)^2], \text{ and}$$

$$1 - P_{n,n+1} = n^2(n+1)^2(1-f)^2 / [n^2(n+1)^2(1-f)^2 + 4(V_{J-n,J-n-1}^0)^2].$$

After computing the probabilities for the highest-energy frustrated channel, one moves to the next frustrated channel (if there is one) and computes  $P_{n+1,n+2}$  in the same manner.

As stated above, flux that does not "hop" to one lower  $j$ -value at a given crossing remains on the higher diabatic curve. Once on this curve, its amplitude must still tunnel through the remaining classically forbidden region; this tunnelling further reduces the probability of eventually exiting in this product channel by an amount  $\exp(-2\kappa L)$ . Here,  $L$  is the "extra distance" that the electron must tunnel from  $R_{J-n,J-n-1}$  to where it exits the classically forbidden region on the  $E^0_{J-n,n}(R)$  diabatic potential. The latter distance can be calculated by first expressing the dipole-bound state energy  $E$  as above:  $E = b(J-n)(J-n+1) + fnb(J-n)$ . Here,  $b(J-n)(J-n+1)$  is the asymptotic energy of the  $j=J-n$  frustrated-channel state and  $nb(J-n)$  is the energy gap between this asymptote and the  $E_{J-n,J-n-1}$  crossing energy. Thus,  $f$  characterizes the fraction of the way between the asymptote and the frustrated-crossing energy. Setting this energy equal to  $b(J-n)(J-n+1) + n(n+1)/2R^2$  yields the value of  $R$  at which flux exits the classically forbidden energy on  $E^0_{J-n,n}(R)$ :

$$R_{\text{exit}} = \{(n+1)/(2b(J-n)f)\}^{1/2}.$$

The  $\kappa$  value is given by

$$\kappa = \{2m[E_{\text{barrier}} - E]\}^{1/2},$$

where  $E_{\text{barrier}}$  is the potential through which the electron is tunnelling between  $R_{J-n,J-n-1}$  and  $R_{\text{exit}}$ . The resultant tunnelling correction  $\exp(-2\kappa L)$  is then calculated as:

$$X_n(f) = \exp\{-2(n(n+1))^{1/2} [((1-f)/f)^{1/2} - (1-f)^{1/2}]\}.$$

Clearly, as the fraction  $f$  approaches zero (i.e., when the channel is barely open),  $X_n$  approaches zero; little flux is able to tunnel through the  $E^0_{J-n,n}(R)$  potential to yield products in the  $j=J-n$  channel. In contrast, when  $f$  approaches unity,  $X_n$  approaches unity and all the flux that remains on the  $j=J-n$  diabatic surface yields product in this channel.

As shown below, the product yield for the channel with  $j=J-n$  is  $(1 - P_{n,n+1})X_n$ . For the frustrated channel with  $j=J-n-1$ , the yield is

$P_{J-n, J-n-1}(1 - P_{J-n-1, J-n-2})X_{n+1}$  - the fraction that hopped to  $j=J-n-1$  at the first crossing and subsequently remained on  $j=J-n-1$  at the second frustrated crossing. The fraction  $P_{J-n, J-n-1} P_{J-n-1, J-n-2}$  is predicted to have exited the second crossing on  $j=J-n-2$ . This recursive process is continued until the first open, non-frustrated channel is reached (i.e., the first channel  $j=J-n^*$  for which  $E$  exceeds  $E_{J-n^*, J-n^*-1}$ ).

#### B. Open Non-Frustrated Channels

Once a channel for which  $E$  lies above the crossing energy is encountered, the Landau-Zener (LZ) method can be employed to calculate subsequent hopping probabilities. The fact that the potential  $V(R, \theta)$  depends on  $\theta$  as  $\cos(\theta)$  implies that flux with  $j=J-n$ ,  $l=n$  can "hop" to the  $j=J-n-1$ ,  $l=n+1$  surface or remain on the  $j=J-n$ ,  $l=n$  surface. That fraction of the flux which remains on the  $j=J-n$ ,  $l=n$  surface must remain on this surface all the way to  $R = \infty$  because the potential  $V(R, \theta)$  can not couple  $j=J-n$ ,  $l=n$  to  $j=J-n-2$ ,  $l=n+2$  or to any other diabatic surface which it encounters via crossings at larger  $R$  values. That fraction of the flux that "hopped" to the  $j=J-n-1$ ,  $l=n+1$  surface can, at the next crossing of diabatic surfaces, either remain on this surface (again, all the way to  $R=\infty$  because the potential can no longer couple  $j=J-n-1$ ,  $l=n+1$  to other diabatic states) or hop to the  $j=J-n-2$ ,  $l=n+2$  surface. This progression of surface hoppings proceeds all the way to the  $j=1$ ,  $l=J-1$  and  $j=0$ ,  $l=J$  crossing. At successive crossings, the couplings grow weaker because of the  $1/R^2$  dependence of  $V(R, \theta)$ .

Within the Landau-Zener method<sup>6</sup>, the probability ( $P_{n, n+1}$ ) for "hopping" from the diabatic surface with  $j=J-n$ ,  $l=n$  to that with  $j=J-n-1$ ,  $l=n+1$  is given in terms of matrix elements ( $V_{J-n, J-n-1}$ ) of the potential  $V(R, \theta)$  between the two appropriate angular basis states, the difference in "slopes" ( $\Delta S_{n, n+1}$ ) of the two crossing diabatic surfaces at the crossing point ( $R_{J-n, J-n-1}$ ) and the classical radial velocity of the electron ( $dR/dt_{n, n+1}$ ) at the crossing:

$$P_{n, n+1} = 1 - \exp(-Q), \text{ where}$$

$$Q = |V_{J-n, J-n-1}|^2 / \{h (dR/dt_{n, n+1}) |\Delta S_{n, n+1}|\}.$$

Within the original Clary model, the crossing points and slope differences can be computed and are given by:

$$R_{J-n, J-n-1} = \{(n+1)/2b(J-n)\}^{1/2} \text{ and}$$

$$\Delta S_{n, n+1} = 2(n+1) \{2b(J-n)/(n+1)\}^{3/2}.$$

The potential coupling matrix elements  $V_{J-n, J-n-1}$  are given by Clary as<sup>1a</sup>:

$$V_{n,n+1} = (\mu/R^2) \{ (2(J-n)+1) (2(J-n-1)+1)(2n+1)(2(n+1)+1) \}^{1/2}$$

$$(-1)^{-J-n} \begin{pmatrix} n & n+1 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J-n & J-n-1 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J-n-1 & n+1 & J \\ n & J-n & 1 \end{Bmatrix}$$

where the 3-j and 6-j symbols arise from coupling the angular momenta of the initial and final states through that carried by the  $\cos(\theta)$  component of  $V(R,\theta)$ . These angular momentum factors can be expressed explicitly and give:

$$V_{n,n+1} = 0.20 \mu \text{Debyes} \{ (n+1)(J-n)/((n+3/2)(J-n+1/2)) \}^{1/2}/R^2.$$

The radial velocity at the crossing point  $R_{J-n,J-n-1}$  is given in terms of the total energy  $E$  of the detaching state and the functional form of the diabatic curve  $E^0_{J-n,n}(R)$  :

$$\begin{aligned} (dR/dt_{n,n+1}) &= \{ 2[ E - b(J-n)(J-n+1) - n(n+1)/2R^2 ] \}^{1/2} \\ &= \{ 2[ E - b(J-n)(J+1) ] \}^{1/2}. \end{aligned}$$

As noted above, only those final states  $j=J-n$  with  $b(J-n)(J+1) > E$  can be examined using the LZ approach as outlined here. The hopping probabilities involving frustrated open channels are computed using the perturbative approach detailed earlier.

### C. Product-Channel Yields

The probability that the system hops to the diabatic curve with one lower  $j$  value is  $P_{n,n+1}$  ; the probability that it remains on the incoming diabatic curve (and thus proceeds all the way to  $R=\infty$  on this curve) is  $1-P_{n,n+1}$ . Thus, given knowledge of the highest-energy open channel (call it  $J_i$ ), one evaluates  $P_{n,n+1}$  for  $n=J-J_i$ . If  $J_i$  is frustrated, then the perturbative equations are used; else, the LZ expressions are employed. The total yield of neutrals in rotational state  $J_i$  is given by this  $1-P_{n,n+1}$  (multiplied by  $X_{J-J_i}$  if this channel is frustrated). For the  $P_{n,n+1}$  fraction that hop to the  $j=J-n-1$  diabatic curve (i.e., to the diabatic curve with one lower  $j$  value), one computes  $P_{n+1,n+2}$ , and evaluates the yield of neutrals in  $J_i-1$  as  $P_{n,n+1} (1-P_{n+1,n+2})$  (multiplied by  $X_{J-J_i-1}$  if this channel is also frustrated). For the  $P_{n,n+1} P_{n+1,n+2}$  fraction that hopped to the  $n+2$  curve, one computes  $P_{n+2,n+3}$  and evaluates the yield of neutrals in  $J_i-2$  as  $P_{n,n+1} P_{n+1,n+2} (1-P_{n+2,n+3})$  (multiplied by  $X_{J-J_i-2}$  if this channel is also frustrated). This recursive process is continued until one reaches the last crossing. The general formula for production of neutrals in level  $J_i-k = J-n-k$  is:

$$Y(J_i-k) = \{ \prod_{l=1,k} P_{n+l-1,n+l} \} (1 - P_{n+k,n+k+1}) X_{J-J_i-k},$$

where the  $X_{J-J_i-k}$  are the tunnelling corrections that apply only to frustrated open channels that occur. This procedure gives the

fraction of detaching anions that begin in dipole-bound state  $J$  that end up in neutral-molecule state  $J_i-k$ , where  $k$  ranges from 0 through  $J_i$  (when  $k=J_i$ , the yield formula is  $\{\prod_{l=1,k} P_{n+1-l,n+1}\}$ ), with  $J_i$  being the first (frustrated or not) open channel.

## VI. Rate Enhancements Near Channel Openings

As one passes through spectral regions where new  $\Delta J$  values open (e.g., for several  $J$  values,  $\Delta J=2$  may be open but  $\Delta J=1$  is closed; then, at higher  $J$ ,  $\Delta J=1$  opens), the rate of detachment is often observed to undergo significant increases. The original rotationally adiabatic model is able to reproduce many of the trends in lifetimes in terms of the dependence of  $E_0(R)$  (in particular, the tunnelling barrier width and height) on rotational quantum numbers. However, there seem to be effects that arise in the neighborhoods of channel openings which require extension of the model.

To understand these effects, consider a situation in which the dipole-bound state energy  $E_{J-1}$  lies just below the  $J-n-1$  state of the neutral but the anion's state  $E_J$  lies just above the  $J-n$  state of the neutral; in this case,  $\Delta J$  changes from  $n+1$  to  $n$  as the anion moves from  $E_{J-1}$  to  $E_J$ . The qualitatively important effect which the original rotationally adiabatic model neglects has to do with the fact that the neutral state  $J-n$  is a "frustrated" state when the dipole-bound state's quantum number is  $J$  (in fact,  $J-n-1$  and others may also be frustrated if their crossing energies  $E_{J-n-1,J-n-2}$ , etc. lie higher than the dipole-bound state's energy). In moving from a closed channel to a frustrated channel, the original model makes no qualitative change in its ionization-rate predictions, which remain governed purely by the rate of tunnelling through  $E_0(R)$ . The original model has the open but frustrated channels contribute no additional effect to the total detachment rate (and gain zero branching yield, as a result) because no tunnelling occurs to  $R$  values beyond their crossing points  $R_{J-n,J-n-1}$ , etc.

Within the frustrated-channel picture, amplitude on the neutral's frustrated states are present in amounts which are estimated by perturbation methods. This analysis also gives an estimate of the fractional increase in the detachment rate to be expected as one experiences a new channel opening. In the above example just prior to the channel opening when the dipole-bound state's quantum number is  $J-1$ , the state lying just above  $E$  (i.e., the  $j=J-n-1$  state for which  $\Delta J = n$  in the above example) is closed; only the fraction  $P_{n+1,n+2}$  in the  $j=J-n-2$  state continues on to eventually detach in  $J-n-2$ ,  $J-n-3$ , etc. After the opening when the dipole-bound

state quantum number is  $J$ , both the corresponding fraction ( $P_{n,n+1}$ ) and the fraction  $(1 - P_{n,n+1})X_n$  remaining on the new open channel  $j=J-n$  eventually detach. Thus, the rate ratio is given by:

$$\text{rate}_j/\text{rate}_{j-1} = [(1 - P_{n,n+1})X_n + (P_{n,n+1})]/P_{n+1,n+2}.$$

The original rotationally adiabatic model ignores the fraction  $(1 - P_{n,n+1})X_n$  that detach via the frustrated channel and counts only the fraction  $P_{n,n+1}$  that detach after hopping to  $j=J-n-1$ . For the dipole-bound state  $E_j$  in which  $j=J-n$  is frustrated, the predictions of the original model must therefore be scaled by the ratio:

$$\begin{aligned} \text{rate}_j/\text{rate}_{j,\text{adiabatic}} &= [(1 - P_{n,n+1})X_n + (P_{n,n+1})]/P_{n,n+1} \\ &= 1 + \{n^2 (n+1)^2 (1-f)^2/4(V_{J-n,J-n-1}^0)^2\} \\ &\quad \exp\{-2(n(n+1))^{1/2} [((1-f)/f)^{1/2} - (1-f)^{1/2}]\} \\ &= 1 + \{n^2(n+1)(1-f)^2(n+3/2)(J-n+1/2)/((J-n)\mu^2_{\text{Debyes}})\} \\ &\quad \exp\{-2(n(n+1))^{1/2} [((1-f)/f)^{1/2} - (1-f)^{1/2}]\}, \end{aligned}$$

where the expressions given earlier for the hopping probabilities among frustrated channels and for the  $V_{J-n,J-n-1}^0$  have been inserted. In fact, if lower open-channel states are also frustrated (this can occur if their crossing energies lie above  $E$ ), the rate should be scaled by a product of factors as given above where  $n$  is replaced by  $n+k$  and  $k$  is allowed to run over all states  $j=J-n-k$  that are frustrated at energy  $E$ . These scalings are necessary because the original adiabatic model allows only  $P_{n+k,n+k+1}$  of the amplitude entering each of the frustrated crossing points to detach; in reality, all of the amplitude may detach.

## VII. Example Application

To illustrate the effects of the frustrated-channel corrections described here, consider dipole-bound states arising from a molecule with  $\mu = 3.6$  Debyes (this is approximately correct for<sup>1b</sup>  $\text{CH}_2\text{CN}$ ). The exponential tunnelling component of the correction factor varies with  $n$  and  $f$  as shown in Table 2 below. The factor  $W(n,J)/\mu^2_{\text{Debyes}} = 6.465\{n^2(n+1)(n+3/2)(J-n+1/2)/((J-n)\mu^2_{\text{Debyes}})\}$  is given, for various  $n$ , as in Table 3. The overall ratio of the predicted to rotationally adiabatic rates is then given as  $1+T(n,f)W(n,J)/\mu^2_{\text{Debyes}}$ .

It is useful to tabulate quantities in the above manner because, for any given dipole moment  $\mu_{\text{Debyes}}$ , one can easily compute the channel-opening corrections to the RA model in terms of the experimentally observed anion-neutral state energy gap (which determines  $f$ ). For example, consider the  $\Delta K=0$  detachment rates associated with the  $J=31-40$ ,  $K=0$  levels of the dipole-bound state of  $\text{CH}_2\text{CN}^-$ . These states all decay<sup>1b</sup> to neutral-molecule rotational levels with  $\Delta J \geq 3$ . The anion and neutral (with  $\Delta J=3$ ) energy levels for this

system, along with the corresponding  $f$ -values, are given below in Table 4 (here  $n=3$ ).

Using a dipole moment<sup>1b</sup> of  $\mu_{\text{Debyes}} = 3.6$ , the rate ratios shown in the last column are obtained as outlined above. Clearly, as the  $\Delta J=3$  channel becomes open (at  $J=31$ ),  $f$  is small and the corrections to the RA model are minor. As  $f$  increases (i.e., as the  $\Delta J=3$  channel opens more fully), the corrections grow. The qualitatively important feature suggested by these results is that the autoionization rates should increase with  $J$  more rapidly than predicted in the original RA model whenever new channel openings occur. In Figure 2 below, the linewidths estimated by Clary for these transitions and those obtained after applying the above frustrated-channel corrections are shown. The quantitative predictions achieved through these corrections probably become less reliable as the corrections become larger because the perturbative method used to estimate such corrections becomes suspect.

## VII. Summary

Modifications have been made to Clary's original rotationally adiabatic model that treat final-state product yields and rate enhancements near channel openings. The latter are found, in an example calculation chosen to represent rotational autoionization of dipole-bound  $\text{CH}_2\text{CN}^-$  (with  $\text{EA}=60 \text{ cm}^{-1}$  and  $\mu_{\text{Debyes}}=3.6$ ) to produce substantial rate enhancements in the neighborhood of new channel openings. The essential ingredients in this model are the electron binding energy, the dipole moment, and the rotational constants of the molecule. The corrections are tabulated here in a manner that facilitates application to a wide variety of dipole-bound anions. For any anion state  $J$ , if the  $\Delta J$  value to the first energetically accessible neutral-molecule state and the anion-neutral state energy difference are known, then  $T(n,f)$  and  $W(n,J)$  can easily be calculated. The tables provided here then permit easy evaluation of the corrections to the rotationally adiabatic rates.

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2. An analogous treatment for symmetric top molecules coupled to a dipole-bound electron is contained in Clary's original works<sup>1a</sup>; for pedagogical purposes, emphasis is placed here on the diatomic-molecule case where the notation is less complicated. The enhancements to the original Clary model introduced here for the diatomic-molecule case apply equally well to the symmetric top and other situations.

3. Smaller contributions from  $j=J-2, l=2$ ,  $j=J-3, l=3$ , and so on are, of course, also present in this hybrid at these R-values.

4. For small  $n$ , this places the crossing between the the neutral's (J-n) and (J-n+1) states; however, for  $n \geq 3$  the crossing can occur above even the (J-n+1) state.

5. The experimentally observed small differences in the rotational constants of the neutral and the dipole-bound anion, caused by geometrical differences induced by the "extra" electron's bonding or antibonding effects, give rise to progressions of rotational energy levels which are not adequately described within the above picture. For example, if the neutral molecule has a  $b_v$  value ( $b^0$ ) which is slightly larger than that of the dipole-bound anion ( $b^-$ ) and this state of the anion is bound by EA, then the pattern of neutral and anion states with energies

$$E^0_J = b^0 J(J+1) \text{ and}$$

$$E^-_{J'} = b^- J'(J'+1) - EA$$

gives rise to a situation in which the lowest states of the anion that can detach can involve relatively large  $\Delta J$ . As  $J'$  is increased, the values of  $\Delta J$  then decrease (because the neutral's rotational energy level ladder moves faster than does the anion's). However, as one moves to higher and higher  $J'$ , there is a minimum value (whose value depends on EA,  $b^-$ , and  $b^0$ ) which  $\Delta J$  achieves; after this minimum value,  $\Delta J$  increases with increasing  $J'$ . Thus, unlike the  $b^0=b^-$  case, one need not realize  $\Delta J = 1$  at all.; if EA is large, the minimum  $\Delta J$  can be quite large, in which case detachment will be

slow for all  $J'$  states. In contrast, if  $b^-$  is slightly larger than  $b^0$ , the lowest states of the dipole-bound anion that can detach undergo larger  $\Delta J$  transitions. As  $J'$  increases, smaller and smaller  $\Delta J$  values are realized. Eventually  $\Delta J = 0$  transitions open, and at even higher  $J'$  values,  $\Delta J$  becomes negative ( i.e., transitions in which the neutral is in a higher rotational level than the anion occur) and becomes even more negative as  $J'$  further increases. Unlike the  $b^0 = b^-$  case,  $\Delta J = 0$  and even negative  $\Delta J$  values are realized here.

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### Figure Captions

Figure 1. Rotationally diabatic and adiabatic potentials for neutral-molecule rotor and electronic angular momenta  $j,l = 34,0; 33,1; 32,2; 31,3; 30,4; 29,5; 28,6; \text{ and } 27,7$  for  $\text{CH}_2\text{CN}^-$  with  $K=0$ . The anion level  $J=34$  is also shown. See text for details.

Figure 2. Linewidths in Mhz for  $\text{CH}_2\text{CN}^-$  for  $J=31$  to  $39$  within Clary's adiabatic model and the present corrected model.

Table 1  
 Anion and Neutral Rotational Energies ( $\text{cm}^{-1}$ ) for  $\text{CH}_2\text{CN}^-$ ,  $K=0$ ;  
 $b=0.341 \text{ cm}^{-1}$ ,  $\text{EA}=60 \text{ cm}^{-1}$

Anion	Neutral	J	$\Delta J^a$
-60	0	0	-
-58	2	2	-
-53	7	4	-
-46	14	6	-
-35	24	8	-
-22	38	10	-
-7	53	12	-
12	72	14	5
33	93	16	5
57	117	18	5
83	143	20	5
113	173	22	5
145	205	24	4
179	239	26	4
217	277	28	4
257	317	30	4
301	360	32	3
346	406	34	3
394	454	36	3
445	505	38	3

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 a.  $\Delta J$  is the change in J accompanying a transition from this J-level of the anion to the first energetically accessible state of the neutral.

Table 2  
 $T(n,f)$  Factors for  $\Delta J=n$  Values from 1 to 4 and  $f$ -Values from 0.1 to 1

$f=$	$T(n,f)=(1-f)^2 X_n(f)$			
	$n=1$	$n=2$	$n=3$	$n=4$
0.1	$2.4 \times 10^{-3}$	$3.5 \times 10^{-5}$	$5.5 \times 10^{-8}$	$9 \times 10^{-9}$
0.2	0.027	$3.8 \times 10^{-3}$	$3 \times 10^{-4}$	$3 \times 10^{-5}$
0.3	0.070	0.017	0.004	0.001
0.4	0.100	0.040	0.016	0.006
0.5	0.110	0.060	0.034	0.019
0.6	0.096	0.066	0.046	0.032
0.7	0.066	0.053	0.042	0.034
0.8	0.035	0.031	0.028	0.026
0.9	0.010	0.009	0.009	0.008

Table 3  
 $W(n,J)/\mu^2$  Factors for  $\Delta J=n$  from 1 to 4

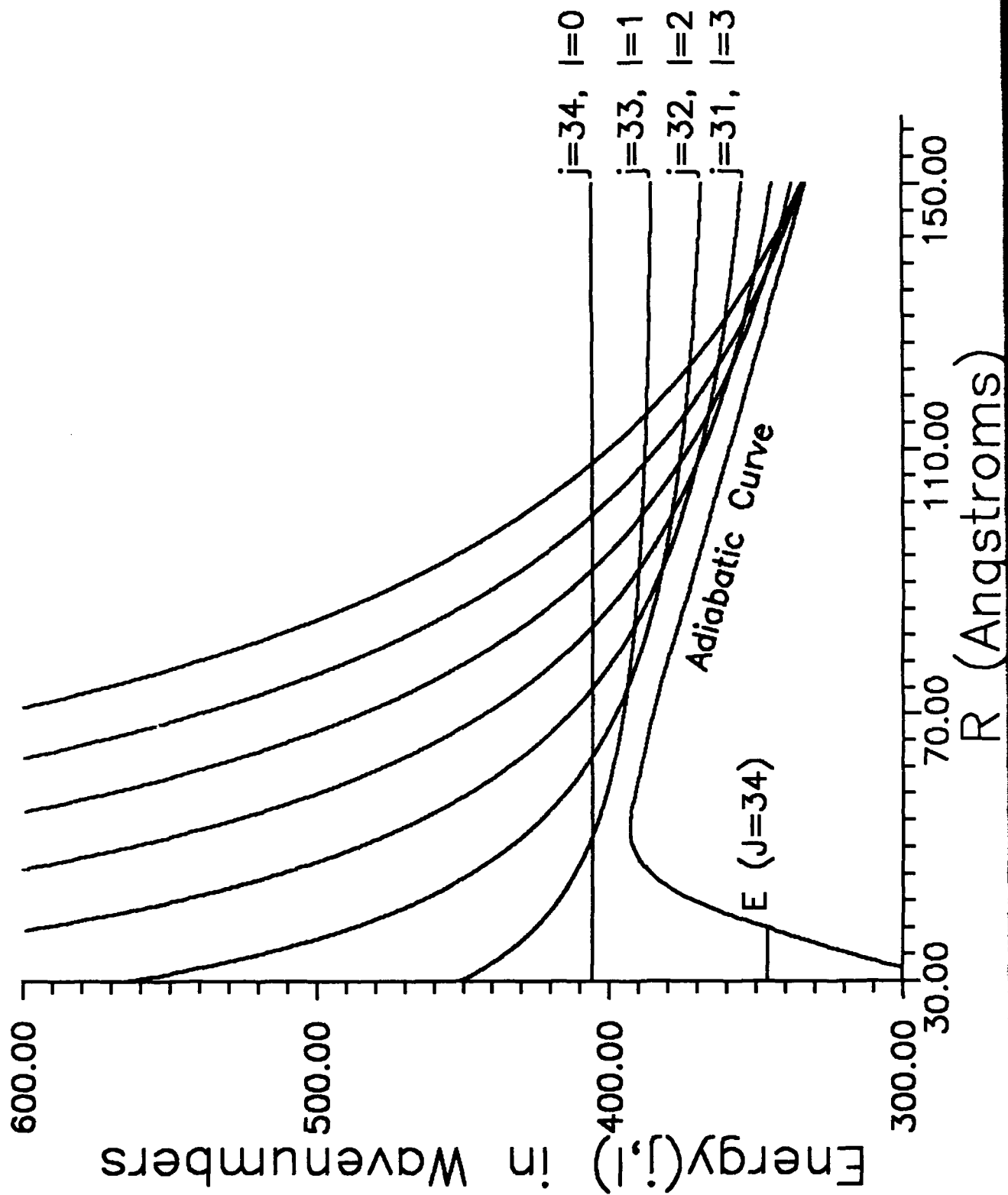
$n=1$	$32 (J-0.5)/[\mu^2 \text{Debyes}(J-1)]$
$n=2$	$271 (J-1.5)/[\mu^2 \text{Debyes}(J-2)]$
$n=3$	$1047 (J-2.5)/[\mu^2 \text{Debyes}(J-3)]$
$n=4$	$2845 (J-3.5)/[\mu^2 \text{Debyes}(J-4)]$

Table 4  
Anion&Neutral Energies ( $\text{cm}^{-1}$ ), f-Values, and Rate Ratios for<sup>a</sup>  $\text{CH}_2\text{CN}^-$

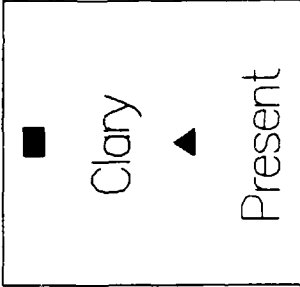
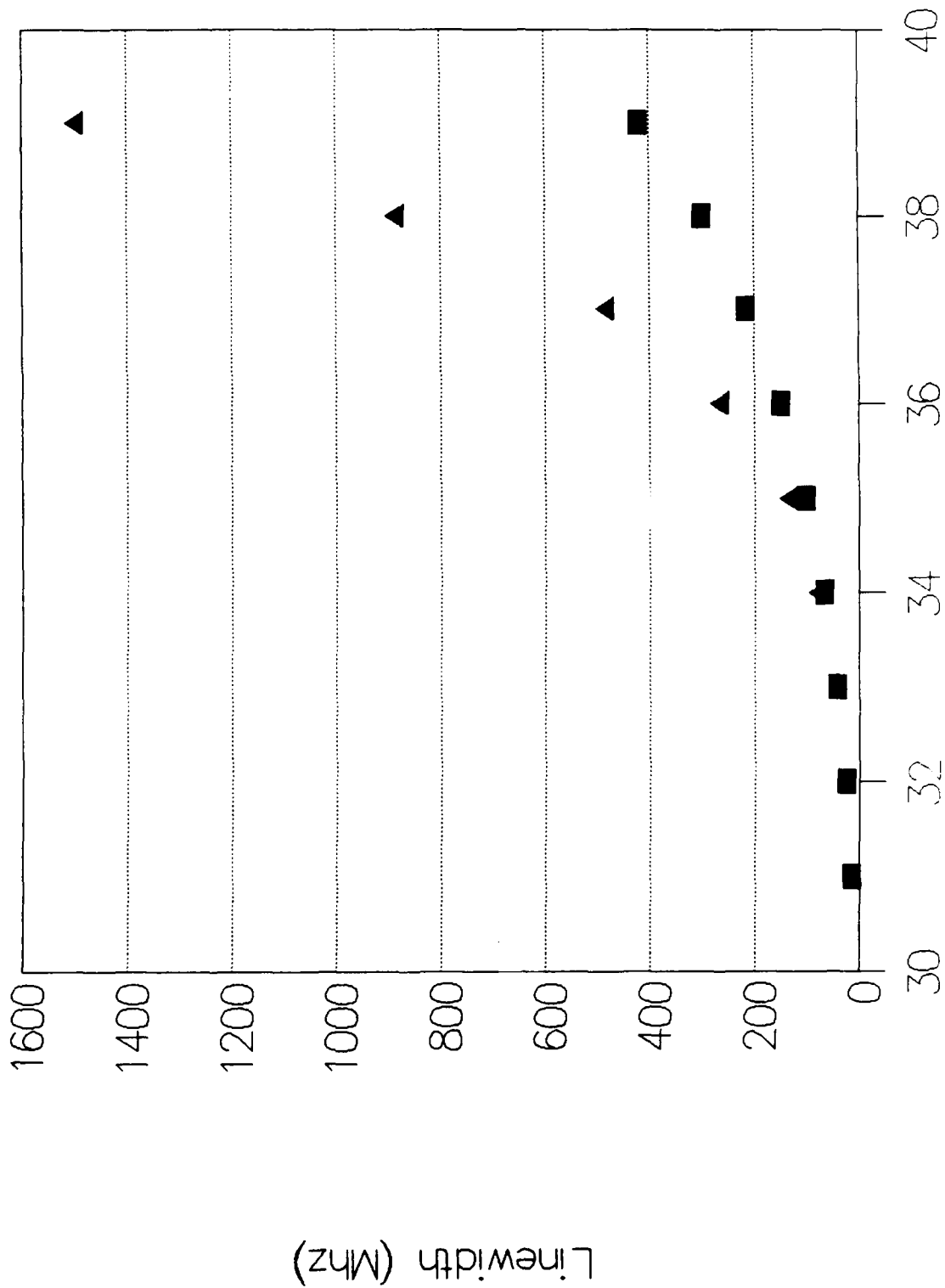
Anion J value	Anion Energy	Neutral Energy	f- Value	Rate Ratio <sup>b</sup>
31	278.27	276.89	0.05	1.00
32	300.10	296.67	0.13	1.00
33	322.60	317.13	0.18	1.02
34	345.79	338.27	0.24	1.16
35	369.66	360.10	0.29	1.31
36	394.21	382.60	0.34	1.78
37	419.45	405.79	0.39	2.25
38	445.36	429.66	0.44	2.96
39	471.96	454.21	0.48	3.57
40	499.24	479.45	0.52	4.04

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 a. A pseudo-diatomic b value of  $0.341 \text{ cm}^{-1}$  and an EA of  $60 \text{ cm}^{-1}$  were used to compute these energy levels. They correspond to  $K'=0 \Rightarrow K=0$  transitions of the nearly symmetric-top  $\text{CH}_2\text{CN}^-$  species. For all anion-to-neutral transitions,  $\Delta J=3$ , so the neutral J is equal to the tabulated anion-J minus 3.

b. Defined as  $1+T(n,f)W(n,J)/\mu^2_{\text{Debyes}}$ , this is the "corrected"-to-rotationally-adiabatic rate ratio.  
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# Linewidths (Mhz)



Anion J-Value