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Temperature and kinetic energy dependences of the rate constant for the reaction $^{22}Ne^{+}+^{20}Ne$

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Rate constants for the reaction $^{22}Ne^{+}+^{20}Ne \rightarrow ^{20}Ne^{+}+^{22}Ne$ have been measured as a function of average center-of-mass kinetic energy ($\langle E_{c.m.}\rangle$) at each of three temperatures: 193, 296, and 464 K. The measurements were made in the range of $\langle E_{c.m.}\rangle$ from 0.02 to 1 eV. The temperature dependence of the rate constant was determined for the first time and is of the form $T^{0.29}$. The rate constants measured as a function of $\langle E_{c.m.}\rangle$ at the different temperatures depend only on $\langle E_{c.m.}\rangle$ and not on experimental temperature for a given $\langle E_{c.m.}\rangle$, as expected. Measured reduced mobilities are also reported for $^{22}Ne^{+}$ drifting in He. Classical trajectory calculations of the rate constants have been performed using the probability function of Rapp and Francis [J. Chem. Phys. **37**, 2631 (1962)], and Dewangen [J. Phys. B **6**, L20 (1973)] [as corrected by Gerlich (private communication)] as a function of internuclear separation. The theoretical rate constants are 10–30% higher than the measured values.

I. INTRODUCTION

Symmetric charge-transfer reactions between rare-gas positive ions and their parent atoms have been studied for several decades. These reactions are of particular interest due to their relatively large cross sections at high collision energy. The rate constants for these reactions can exceed the capture limiting values.[1,2] The reactions, which are efficient routes for effective momentum transfer, are also interesting because they are responsible for the low mobilities of rare-gas cations in their parent gases.[3]

In the present study, the rate constant for

$$^{22}Ne^{+}+^{20}Ne \rightarrow ^{20}Ne^{+}+^{22}Ne \tag{1}$$

was measured as a function of ion–neutral-atom average-center-of-mass kinetic energy ($\langle E_{c.m.}\rangle$) at several temperatures using a variable-temperature selected-ion-flow drift tube (VT SIFDT) instrument. The rate constant for this reaction at room temperature has been determined previously in a selected-ion-flow tube (SIFT) apparatus[4] and estimated from ion residence times in a mass-spectrometer ion-source experiment.[5] Reaction cross sections have been measured as a function of ion kinetic energy in drift tube,[6] triple quadrupole mass spectrometer,[7] and ion-beam experiments.[8–14] We report here the temperature dependence of the rate constant k_1 for reaction (1) and $\langle E_{c.m.}\rangle$ dependences of k_1 measured at different temperatures.

The reason for undertaking this study was, in part, as a check of the part of the experimental technique in which dependences of rate constants on $\langle E_{c.m}\rangle$ are measured at different temperatures. In the experiment, the value of $\langle E_{c.m.}\rangle$, calculated from the Wannier formula,[15] depends on contributions from both the temperature and the ion kinetic energy imparted by the electric drift field (in the ion–neutral-reactant center-of-mass frame

$$\langle E_{c.m.}\rangle = [(m+M)m_n v_d^2]/[2(m+m_n)] + \tfrac{3}{2}k_B T ,$$

where m is the mass of the ion, M is the mass of the buffer gas, m_n is the mass of the neutral reactant, k_B is Boltzmann's constant, and v_d is the drift velocity). A given $\langle E_{c.m.}\rangle$ can be reached by employing various combinations of ion energy and temperature. For a reaction between a monatomic ion and a monatomic neutral reactant, varying the temperature has essentially the same effect as varying the ion kinetic energy with the drift field; both lead to changes in translational energy only, since there are no internal degrees of freedom (ion speed distributions in He are approximately Maxwellian in the drift tube[16,17]). Therefore, for atomic reactants, $\langle E_{c.m.}\rangle$ dependences of rate constants measured at different temperatures are expected to lie on a single curve. For polyatomic reagents, internal excitation of both ion and neutral reactants can occur due to temperature, and additional internal excitation of the ion can arise from increased ion-buffer collision energy due to the drift field. In this case, rate constants measured at a particular $\langle E_{c.m.}\rangle$, but at different temperatures might differ due to effects of the varying amounts of internal excitation in the reactants at the different temperatures and drift field strengths that combine to give the same $\langle E_{c.m.}\rangle$.[18–20]

II. EXPERIMENT

The experiments were performed using a variable-temperature selected ion flow drift tube apparatus at the Geophysics Laboratory at Hanscom Air Force Base, shown schematically in Fig. 1. The apparatus and technique have been described in detail elsewhere.[20] Only details pertinent to the present study are given here. The $^{22}Ne^+$ ions were generated by electron impact on unlabeled neon (90.9 at. % ^{20}Ne and 8.8 at. % ^{22}Ne) in a high-pressure (0.1–1 Torr) ion source. The ions with mass-to-charge ratio (m/e) equal to 22 daltons were then mass-selected in quadrupole mass spectrometer and injected into the flow tube through a Venturi inlet. Inside the flow tube the ions were entrained in a fast flow ($\sim 10^4$ cm/s at 0.4 Torr) of helium buffer gas. The neutral reactant ^{20}Ne was introduced downstream and reacted with the ions over a known distance. The reactant and product ions were mass-analyzed in a second quadrupole mass spectrometer and detected by a channel particle multiplier. Rate-constant measurements were made as a function of $\langle E_{\text{c.m.}} \rangle$ at each of three temperatures by varying the electric field in the drift-tube portion of the flow tube.

The rate constants were extracted from least-squares fits of the natural logarithm of the $^{22}Ne^+$-ion signal plotted versus the concentration of added ^{20}Ne reactant gas for a known reaction time. The reaction time was determined from ion velocity measurements at each temperature and each drift-tube electric-field strength. The ion velocity was determined by imposing a pulsed retarding potential on a drift-tube guard ring and then measuring the arrival time of the perturbation in the ion swarm at the detector using a digital time-of-flight unit and a multichannel analyzer. This procedure was repeated at a second guard ring in order to subtract the contribution from downstream end effects. The above method was also used at zero drift field in order to measure the zero-field ion velocity. The drift velocity v_d is equal to the ion velocity minus the zero-field ion velocity. The ion mobility μ is calculated from the relation $\mu = v_d / E$ where E is electric drift-field strength. The reduced mobility μ_0 is defined as $\mu_0 = \mu(\mathcal{P}/760)(273.16/T)$ where $\mathcal{P}$ is the buffer gas pressure in torr and T is the temperature in kelvin.

The experimental temperature of 193 K was achieved by circulating liquid nitrogen through a heat exchanger in contact with the flow tube. Electrical heaters attached to the heat exchanger raised the temperature of the flow tube to 464 K.

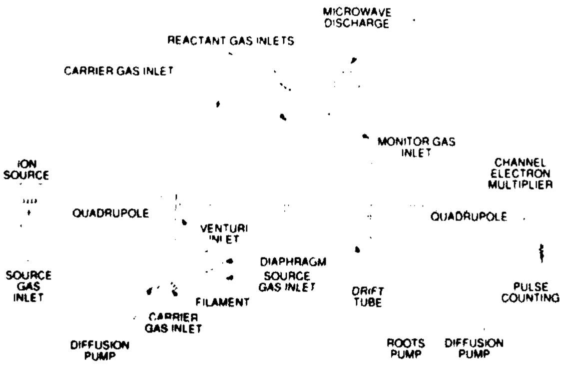

FIG. 1. Schematic diagram of the variable-temperature selected-ion-flow drift tube (VT-SIFDT) apparatus at the Geophysics Laboratory at Hanscom Air Force Base.

It has been assumed in this work that either the charge-transfer rate constants for the $Ne^+({}^2P_{3/2})$ and $Ne^+({}^2P_{1/2})$ spin-orbit states are equal, or that only the ground state $Ne^+({}^2P_{3/2})$ is present in the flow. The energy difference between the two states is 97 meV. The primary ion decay plots were linear over as much as two orders of magnitude of ion count rate, indicating no evidence for the presence of two states reacting at significantly different rates. The variation of the injection energy of the ion into the flow tube caused no change in the results. Drift-tube measurements of Ne^+ in Ne at 77 K by Helm and Elford[21] showed that the mobilities of the two states (which are controlled by the rate constants for charge transfer) are different below $E/N = 39$ Td but by less than 10%. The zero-field reduced mobilities of the two states also differ by less than 10%.[21]

Another possible source of interference in the kinetics measurements is the formation of cluster ions with the He buffer, followed by reaction of the cluster ions with Ne. The rate constant for the reaction

$$Ne^+ + 2He \rightarrow NeHe^+ + He \tag{2}$$

is 2.0×10^{-32} cm^6 s^{-1} at 300 K and 8.7×10^{-32} cm^6 s^{-1} at 120 K.[22] A subsequent switching reaction

$$NeHe^+ + Ne \rightarrow Ne_2{}^+ + He \tag{3}$$

can occur; the rate constant for this process is 1.4×10^{-10}cm^3 s^{-1}.[23] The initial experiments included runs at 86 K, but the presence of the ions $NeHe^+$ and $Ne_2{}^+$ was detected. At 193 K, the sum of the count rates from cluster ions was less than 2% of the total-product ion count rate. At the higher temperatures the contribution from clusters was negligible or zero.

An interesting observation made during the course of the experiments was that a very small signal from an ion at m/e equal to 20 daltons was present when the ^{20}Ne neutral flow was turned off. The source of this $^{20}Ne^+$ was an 8-ppm impurity of Ne in the high-purity helium carrier gas used, revealed by analysis of the He. The concentration of impurity was low enough so as not to affect significantly the rate-constant measurements.

Several additional checks were performed, including the use of different isotopic purities of the Ne neutral reactant, and studying the reverse of reaction (1), the reaction of $^{20}Ne^+$ with ^{22}Ne. These tests gave the same results as those obtained in the basic experiment described here.

The gases used were unlabeled Ne (purified, 99.99%), ^{20}Ne (99.95% isotopic purity), ^{22}Ne (99.9% isotopic purity), and He (high purity, 99.997%). The gases were used without further purification.

III. THEORY OF SYMMETRIC RESONANT CHARGE TRANSFER

The theoretical rate-constant calculation is based on the charge-transfer probability function used by Rapp and Ortenburger,[24] Rapp and Francis,[25] and Dewangan[26] (as corrected by Gerlich[27]) for symmetric resonant charge-transfer processes,

$$A+A^{+}\rightarrow A^{+}+A\ . \tag{4}$$

The probability of transition from the initial unperturbed state to the final unperturbed state is given by

$$\mathfrak{P}_{i\text{-}f}=\sin^{2}\left[\int_{-\infty}^{+\infty}\frac{E_a-E_s}{2\hbar}dt\right]\ , \tag{5}$$

where E_s and E_a are the energies of the symmetric and antisymmetric stationary states, respectively. E_a-E_s was calculated by Rapp and Francis[25] and Dewangan[26] and corrected by Gerlich[27] to be

$$E_a-E_s=\tfrac{8}{3}I(R/0.529)\exp[-(I/13.6)^{1/2}R/0.529]\ , \tag{6}$$

where I is the ionization potential of A in electron volts and R is the separation of A^{+} and A in angstroms.

It should be noted that Eq. (6) was derived from an analysis of the A_2^{+} collision complex as a one-electron problem.[25] It is good only for the $H^{+}+H$ system. For the $Ne^{+}+Ne$ system being considered here, Eq. (6) is a gross approximation. Not only is this a multiple-electron system, but also the Ne^{+} ion is a P state rather than an S state. Thus there is more than one E_a-E_s pair in this system, for which Eq. (6) does not take account. However, as pointed out by Rapp and Francis,[25] Eq. (6) does roughly correlate the size of an orbital with the ionization potential, which is sufficient for approximate calculations.

Rapp and Francis assumed rectilinear orbits. The probability of charge transfer in a collision with velocity v and impact parameter b is then given by

$$\mathfrak{P}(b,v)=\sin^{2}\left[\int_{-\infty}^{+\infty}\frac{E_a-E_s}{2\hbar v}\,dx\right]\ , \tag{7}$$

and the cross section was calculated from

$$\sigma(v)=2\pi\int_{0}^{\infty}\mathfrak{P}(b,v)b\,db\ . \tag{8}$$

In the present theoretical treatment, the trajectory method[28-30] is used to calculate the charge-transfer rate constants. Instead of assuming rectilinear orbits, the ground-state potential-energy curve, including spin-orbit coupling for Ne_2^{+} calculated by Michels, Hobbs, and Wright,[31] is used to calculate the path of each trajectory. The probability of charge transfer for each trajectory is calculated directly from Eq. (5). To do this, each trajectory is integrated inward from 63 Å, with time intervals of 2×10^{-16} s, until the interacting partners separate themselves again to 63 Å.

The charge-transfer rate constant at a given ion-neutral-atom average center-of-mass kinetic energy $\langle E_{\text{c.m.}}\rangle$ is given by

$$k(\langle E_{\text{c.m.}}\rangle)=\frac{4\pi}{(2\mu)^{3/2}\langle E_{\text{c.m.}}\rangle^{1/2}}\int\mathfrak{P}_{i\text{-}f}L\,dL\ , \tag{9}$$

and 5000 trajectories are used for each $\langle E_{\text{c.m.}}\rangle$. A correction is made by comparing the rate constants calculated from the Gerlich[27] formulation with rate constants obtained from trajectory calculations but assuming rectilinear trajectories (i.e., assuming zero potential energy). The charge-transfer rate constant is then obtained by multiplying the present trajectory calculated rate constants by the ratio of the Gerlich results to the rectilinear trajectory results. This correction is necessary for accurate results because the Monte Carlo integration may have a few percent of error. We have also calculated rate constants including the thermal energy distribution. The results are within 2% of those obtained without considering the thermal distribution.

Charge-transfer rate constants were calculated by the trajectory method using the ground- and excited-state potential-energy curves for $Ne_2{}^{+}$ reported by Michels, Hobbs, and Wright.[31] The calculations yielded essentially identical results irrespective of the choice of potential curve. Also, the results are practically the same as (1-2 % lower than) those calculated by Gerlich. The insensitivity of the rate constant to the shape of the potential-energy curve in the $Ne^{+}+Ne$ system is due to the fact that the effect of the potential energy on the motion of the ion-atom pair is significant only at very small ion-atom separation, for which the average charge transfer probability is 0.5. That is, the deviation from rectilinear motion occurs only for very small impact parameters such that the overall charge-transfer rate constant is unaffected. Theoretically, half of the collisions should follow the potential curve for the antisymmetric state. (See Ref. 3, Chap. 6.) However, it is not necessary to take this into consideration here because the trajectory

TABLE I. Measured reduced mobilities μ_0 of $^{22}Ne^{+}$ in He at 193, 296, and 464 K. E/N in units of 1 Td$=10^{-17}$ V cm^{-2}; μ_0 in units of cm^2 V^{-1} sec^{-1}; T_{eff} in units of K. Total pressure: 0.314 Torr at 193 K; 0.417 Torr at 296 K; 0.402 Torr at 464 K.

	193 K			296 K			464 K	
E/N	μ_0	T_{eff}	E/N	μ_0	T_{eff}	E/N	μ_0	T_{eff}
7.99	19.41	221	6.08	19.39	312	14.96	20.02	568
15.98	19.64	307	12.12	19.30	359	29.84	19.74	865
23.90	20.24	464	18.15	20.24	452	44.76	19.27	1324
31.97	20.41	685	24.19	20.00	567	59.82	18.90	1942
40.10	20.62	983	33.27	20.85	852	73.54	18.34	2567
			42.27	20.25	1143			

distortion by the potential is negligible and all of the trajectories can be considered rectilinear. Recently a set of potential energy functions for Ne_2^+ has been reported by Skullerud and Larsen.[32] These potential-energy functions were not used here for the rate-constant calculations because the functions approach negative infinity as the Ne^+-Ne separation approaches zero. This tends to cause a computer overflow at small R. Since the theoretical rate constant is insensitive to the shape of the potential-energy curve, as pointed out above, we feel that it is not necessary to use the Skullerud and Larsen potentials for our calculations.

IV. RESULTS AND DISCUSSION

A. Mobilities

The reduced mobilities of $^{22}Ne^+$ ions drifting in He measured at the three experimental temperatures of 193, 296, and 464 K are tabulated as a function of E/N in Table I. Also given in the table are the effective ion temperatures, T_{eff}, derived[3] from the expression $\frac{3}{2}k_B T_{\mathrm{eff}} = \frac{3}{2}k_B T + \frac{1}{2}Mv_d^2$. This equation is a transformation of the Wannier formula[15] to the ion-buffer center-of-mass frame (note that this is different from the formulation for the ion-neutral reactant center-of-mass frame). It should be noted that the two spin-orbit states of the ions were not resolved in the experiment, and it is uncertain whether or not the excited $^2P_{1/2}$ state was present (see Sec. II).

B. Rate constants

The measured rate constants for reaction (1) are plotted on a log-log scale versus the ion-neutral average center-of-mass kinetic energy $\langle E_{\mathrm{c.m.}} \rangle$ in Fig. 2. The different symbols refer to the three different temperatures at each of which the drift field was varied, generating $\langle E_{\mathrm{c.m.}} \rangle$ dependences at three temperatures. The value of the rate constant measured at 296 K at zero drift field (zero-field) agrees with the SIFT measurement of Jones *et al.*[4] to within 10%. The pure temperature dependence of the rate constant is depicted as a dashed line in the figure. This is a least-squares fit to the three points obtained for zero field at 193, 296, and 464 K. The rate constant was found to be proportional to $T^{0.29}$.

The $\langle E_{\mathrm{c.m.}} \rangle$ dependences measured at the three experimental temperatures all fall on a single curve. This is not an unexpected result since, as stated previously, only translational degrees of freedom of the monatomic reactants can be excited in the experiments. Temperature and drift field have virtually the same simple effect of controlling the $\langle E_{\mathrm{c.m.}} \rangle$. A least-squares fit to the energy-dependent data yielded an $\langle E_{\mathrm{c.m.}} \rangle$ dependence of $\langle E_{\mathrm{c.m.}} \rangle^{0.33}$, in agreement with the temperature dependence within experimental uncertainty.

The calculated rate constants, plotted as a solid line in Fig. 2, vary as $\langle E_{\mathrm{c.m.}} \rangle^{0.41}$, in good agreement with the measured energy dependence. The values of the calculated rate constants are 10–30 % higher than the measured values. While this difference is within the combined accuracies of the experimental and computational methods, it is a systematic difference. Possible sources of systematic error include inadequacy in the approximation of $E_a - E_s$, miscalibration of flow and pressure meters, and error in the time-of-flight measurements.

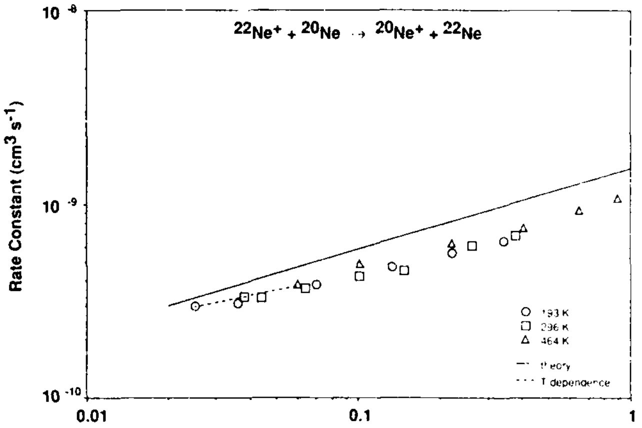

FIG. 2. Rate constants for the charge-transfer reaction of $^{22}Ne^+$ with ^{20}Ne vs ion–neutral-reactant average center-of-mass kinetic energy $\langle E_{\mathrm{c.m.}} \rangle$ measured at three temperatures. The solid line refers to the theoretical rate constant. The dashed line denotes the pure temperature dependence of the measured rate constants.

The increase in the rate constant with increasing temperature and energy ($\langle E_{\mathrm{c.m.}} \rangle$) is attributed to a cross section for charge transfer with only a very slight negative dependence on energy. Increasing the energy (or temperature) leads to an increase in relative velocity proportional to $E^{0.5}$, but leads to only a slight decrease in the cross section. The Langevin value for the rate constant[2] is independent of energy, since the Langevin cross section has an $E^{-0.5}$ energy dependence and average velocity depends on energy as $E^{0.5}$. The present theoretical treatment predicts an energy dependence of the cross section of $E^{-0.09}$. Therefore the calculation predicts the rate constant to be approximately proportional to $E^{0.41}$. The fact that the predicted cross section does have a nonzero, albeit slight, negative energy dependence ($E^{-0.09}$) may be due to a decreasing charge-transfer probability with decreasing time of encounter as energy increases. Results from beam experiments also indicate a weak negative dependence of the cross section for this reaction on collision energy over a very wide energy range,[9–14] from a few eV to energies as high as 100 keV.[13]

The Langevin value of the rate constant is 4.55×10^{-10} $cm^3 s^{-1}$, which should be multiplied by a factor of $\frac{1}{2}$ to account for the symmetric nature of the reaction. Thus the corrected collisional rate constant is $2.27 \times 10^{-10} cm^3 s^{-1}$. The measured rate constants exceed this value over the entire range of experimental temperature and/or energy. This observation is explained by the fact that charge transfer can occur at distances greater than the capture radius. Such behavior is facilitated in this system because here the capture radius is relatively small, due to the low polarizability of Ne. As a result, the collision radius (determined by the repulsive potential between the electron clouds of the ion and neutral reactant) may exceed the capture radius, thus allowing a rate constant in excess of the value based upon the capture radius. This is especially true at high energy, where the capture radius is smallest.

In summary, the rate constants for charge transfer between $^{22}\mathrm{Ne}^+$ and $^{20}\mathrm{Ne}$ were measured as a function of $\langle E_{\mathrm{c.m.}} \rangle$ at 193, 296, and 464 K. The $\langle E_{\mathrm{c.m.}} \rangle$ dependences coincide on a single curve. The rate constant was found to depend on temperature as $T^{0.29}$ and on energy as $\langle E_{\mathrm{c.m.}} \rangle^{0.33}$. Classical trajectory calculations yield an energy dependence of $\langle E_{\mathrm{c.m.}} \rangle^{0.41}$ and rate constant values 10%–30% higher than the measured values.

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[1] Y. Ikezoe, S. Matsuoka, M. Takebe, and A. A. Viggiano, *Gas Phase Ion-Molecule Reaction Rate Constants Through 1986* (Maruzen, Tokyo, 1987).

[2] G. Gioumousis and D. P. Stevenson, J. Chem. Phys. **29**, 294 (1958).

[3] E. A. Mason and E. W. McDaniel, *Transport Properties of Ions in Gases* (Wiley, New York, 1988).

[4] J. D. C. Jones, D. G. Lister, K. Birkinshaw, and N. D. Twiddy, J. Phys. B **13**, 799 (1980).

[5] E. G. Jones and A. G. Harrison, Int. J. Mass Spectrom. Ion Phys. **5**, 178 (1970).

[6] Y. Kaneko, N. Kobayashi, and I. Kanomata, J. Phys. Soc. Jpn. **27**, 992 (1969).

[7] R. I. Martinez and S. Dheandhanoo, Int. J. Mass Spectrom. Ion Proc. **74**, 241 (1986).

[8] B. Ziegler, Z. Phys. **136**, 108 (1953).

[9] J. A. Dillon, Jr., W. F. Sheridan, H. D. Edwards, and S. N. Ghosh, J. Chem. Phys. **23**, 776 (1955).

[10] H. B. Gilbody and J. B. Hasted, Proc. R. Soc. London Ser. A **238**, 334 (1956).

[11] W. H. Cramer, J. Chem. Phys. **28**, 688 (1958).

[12] I. P. Flaks and E. S. Solov'ev, Zh. Tekh. Fiz. **28**, 599 (1958) [Soviet Phys.—Tech. Phys. **3**, 564 (1958)].

[13] P. R. Jones, F. P. Ziemba, H. A. Moses, and E. Everhart, Phys. Rev. **113**, 182 (1959).

[14] P. A. Hamilton and P. F. Knewstubb, Int. J. Mass Spectrom. Ion Proc. **57**, 329 (1984).

[15] G. H. Wannier, Bell Syst. Tech. J. **32**, 170 (1953).

[16] R. A Dressler, H. Meyer, A. O. Langford, V. M. Bierbaum, and S. R. Leone, J. Chem. Phys. **87**, 5578 (1987).

[17] R. A. Dressler, J. P. M. Beijers, H. Meyer, S. M. Penn, V. M. Bierbaum, and S. R. Leone, J. Chem. Phys. **89**, 4707 (1988).

[18] A. A. Viggiano, R. A. Morris, and J. F. Paulson, J. Chem. Phys. **89**, 4848 (1988).

[19] A. A. Viggiano, R. A. Morris, and J. F. Paulson, J. Chem. Phys. **90**, 6811 (1989).

[20] A. A. Viggiano, R. A. Morris, F. Dale, J. F. Paulson, K. Giles, D. Smith, and T. Su, J. Chem. Phys. (to be published).

[21] H. Helm and M. T. Elford, J. Phys. B **10**, 983 (1977).

[22] J. D. C. Jones, D. G. Lister, D. P. Wareing, and N. D. Twiddy, J. Phys. B **13**, 3247 (1980).

[23] D. K. Bohme, N. G. Adams, M. Mosesman, D. B. Dunkin, and E. E. Ferguson, J. Chem. Phys. **52**, 5094 (1970).

[24] D. Rapp and I. B. Ortenburger, J. Chem. Phys. **33**, 1230 (1960).

[25] D. Rapp and W. E. Francis, J. Chem. Phys. **37**, 2631 (1962).

[26] D. P. Dewangan, J. Phys. B **6**, L20 (1973).

[27] D. Gerlich (private communication).

[28] W. J. Chesnavich, T. Su, and M. T. Bowers, J. Chem. Phys. **72**, 2641 (1980).

[29] T. Su and W. J. Chesnavich, J. Chem. Phys. **76**, 5183 (1982).

[30] T. Su, J. Chem. Phys. **82**, 2164 (1985).

[31] H. H. Michels, R. H. Hobbs, and L. A. Wright, J. Chem. Phys. **69**, 5151 (1978).

[32] H. R. Skullerud and P-H. Larsen, J. Phys. B **23**, 1017 (1990).