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The Structure of the Cyclohexyl Radical from State-Selective Photofragment Translational Spectroscopy of the Axial and Equatorial Conformers of Iodocyclohexane

by

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ABSTRACT

Iodocyclohexane ($C_6H_{11}I$) is photodissociated and studied with state-selective photofragment translational spectroscopy. Angular, velocity, and translational energy distributions are obtained for the ground state $I(^2P_{3/2})$ and the excited state $I^*(^2P_{1/2})$ photodissociated iodine atoms. Both states are formed from a one photon absorption that is dominantly parallel to the C-I dissociation coordinate and selectively ionized by 2 + 1 multiphoton absorption for detection. Both a fast and a slow velocity component are observed in the lab velocity distribution for I^* (522±17 and 336±11 m/s, respectively). The relative mass peak intensity is consistent with assigning the fast component to excited iodine atoms produced from the axial conformer of iodocyclohexane, and the slow component from the equatorial conformer. The kinetic energy released in the photodissociation of the axial conformer is 6.0±0.8 kcal/mol greater than that produced from the equatorial conformer. This suggests that the cyclohexyl radical produced from the axial iodocyclohexane has less internal energy than that formed from the equatorial conformer. The conclusion is thus reached that the ground state of the cyclohexyl radical has the hydrogen atom at its radical center in the equatorial position.

INTRODUCTION

Alkyl iodides are known[1] to have an absorption continuum, the so-called A band, in the ultraviolet wavelength region of 200-300 nm. The transition from the ground X state to the A state involves the transition of a non-bonding p electron to an antibonding σ^* molecular orbital.[2] This $\sigma^* \leftarrow n$ transition results in a very fast dissociation of the C-I bond along the repulsive A state[3,4] which produces a ground state alkyl radical and an iodine atom in either a ground state $I(^2P_{3/2})$ or a spin-orbit excited state $I^*(^2P_{1/2})$. For simplicity, these will be referred to as I and I^* respectively. LIF measurements[5] concluded that most of the iodine atoms produced from the photodissociation of iodocyclohexane at 248 nm are in their ground state.

Monosubstituted cyclohexanes are known[6] to exist in two chair conformations, the axial and the equatorial (see figure 1a). These conformers coexist in equilibrium at room temperature with the equatorial form being favored over the axial form due to steric interactions.[6,7] Many spectroscopic and theoretical studies have been carried out on substituted cyclohexanes.[8-18] Thermodynamic data from recent IR/NMR studies[8] indicate that the equatorial conformer of iodocyclohexane, e-$C_6H_{11}I$, is more stable than its axial counterpart, a-$C_6H_{11}I$, by $\Delta G^o=0.61$ kcal/mol. The ratio of IR extinction coefficients for the C-I stretching mode,[8] $\varepsilon_{ax}/\varepsilon_{eq}$, was found to be about 1:4, indicating that the C-I bonds in the different conformers are of different electronic character. Indeed, molecular mechanics calculations[9] and microwave spectroscopy experiments[10] indicate that the different conformers have different C-I bond lengths, with the axial bond length being longer[9,10] by anywhere from 0.005 Å to 0.012 Å. Thus, the C-I bond in the axial conformer should be weaker than that in the equatorial conformer. Theoretical work[20,21] has also been performed on the structure of the cyclohexyl radical. However, there has been disagreement over the stable structure of the radical. *Ab initio* calculations by Lloyd et al.[20] suggest that the radical exists in the chair form with the hydrogen atom at the radical center in the axial position resulting in a structure more stable than that with the same hydrogen in the equatorial position by 0.14 kcal/mol (internal energy difference). In contrast to this, MM2 calculations by Imam and Allinger[21] indicate that the only stable structure for the cyclohexyl radical is one in which the hydrogen at the radical center occupies the equatorial position. Figure 1b illustrates the equatorial and axial configurations of the cyclohexyl radical.

In this work we study the photodissociation of $C_6H_{11}I$ at room temperature using state-selective photofragment translational spectroscopy.[19] The photodissociation reactions studied here are

$$C_6H_{11}I \xrightarrow{h\nu} C_6H_{11} + I^* \qquad (304.02\ \text{nm}) \qquad (1)$$

$$C_6H_{11}I \xrightarrow{h\nu} C_6H_{11} + I \qquad (304.67\ \text{nm}) \qquad (2)$$

With this technique we are able to determine the kinetic energy released in the photodissociation of the iodine atoms produced from the axial and equatorial conformers. It is found that the kinetic energy released from the photodissociation of the axial conformer is higher than that released from the photodissociation of the equatorial conformer by 6.0±0.8 kcal/mol. If the strengths of the C-I bonds in the two conformers are not drastically different from one another, this result suggests that the radical produced from the equatorial conformer has more internal energy than that formed from the axial conformer. This is consistent with predictions[21] that the radical with the hydrogen at the radical center in the equatorial position is the ground state of the cyclohexyl radical.

EXPERIMENTAL

Details of the experimental apparatus and methodology are described elsewhere.[19] Briefly, a single-stage pulsed-acceleration TOF mass spectrometer is used in combination with a linearly polarized pulsed laser(~20 ns). Room temperature vapor of I_2 is used to calibrate the TOF apparatus.[19] At room temperature, iodocyclohexane ($C_6H_{11}I$) vapor is introduced by effusion into the ionization region of the apparatus. The measured pressure in this region is found to be 2.0×10^{-6} torr. Photodissociation of $C_6H_{11}I$ and state-selective ionization of the iodine photofragment are achieved within the same laser pulse. Experiments are performed at two wavelengths, 304.02 nm for I^* (~50 μJ/pulse) and 304.67 nm for I (~25 μJ/pulse), in order to selectively ionize I^* and I via 2-photon resonance plus one photon ionization. Additionally, polarizations parallel and perpendicular to the detection axis ($\alpha = 0^\circ$ and 90°, respectively) were used at each wavelength in order to obtain information about the angular dependence of the photodissociation process. A field-free condition is maintained during a delay time τ of 1.50 μs after the laser pulse. The iodine atoms are then accelerated up toward the detector by applying a pulsed acceleration voltage (approximately -1500 V with a pulse duration of 1.0 μs) to the acceleration electrode. After traveling through a field-free drift region, the ions pass through a discrimination pinhole (6.0 mm diameter) and the TOF distribution is measured. The discrimination pinhole discriminates against photoions with large velocity components perpendicular to the detection axis (velocities in the x and y directions which are greater than 120 m/s).[19]

RESULTS AND DISCUSSION

A. Results

The lab velocity, v_{zl}, distributions observed for different values of the polarization angle, α, are presented in figures 2 and 3 for the I and I^* photofragments, respectively. Both I and I^* exhibit broad velocity distributions, possibly as a result of the high density of vibrational states in the parent molecule since iodocyclohexane is known to have 48 fundamental vibrational modes.[11] While the velocity distribution peaks for I (figure 2) are broad and featureless, they are not as broad for the I^* velocity spectrum (figure 3). This allows for the resolution of a high velocity shoulder from the main peak in the I^* velocity spectrum at $\alpha = 0^o$ (polariztion parallel to the detection axis). Hence, I^* photofragments are being ejected with at least two different energy distributions. The lab velocities in the z-direction, which correspond to peak maxima for the main and shoulder peaks at $\alpha = 0^o$ are $v_{zl,main} = 336 \pm 11$ m/s and $v_{zl,shoul} = 522 \pm 17$ m/s. From figures 2 and 3 the number density of photodissociated iodine atoms produced with the laser polarization parallel to the detection axis is much higher than that produced with perpendicular polarization. This leads to the conclusion that the $A \leftarrow X$ transition is predominantly parallel in both cases, with the values of the anisotropy parameter, β, being: $\beta(I)=1.42 \pm 0.08$, and $\beta(I^*)=0.95 \pm 0.11$ for the main peaks and 1.26 ± 0.14 for the shoulders. This is similar to what is observed for methyl iodide.[3] The anisotropy factor is calulated from the following equation:

$$\beta = (I_{\parallel} - I_{\perp}) /(0.5I_{\parallel} + I_{\perp}) \qquad (3)$$

The intensities ($I_{\parallel}$ for parallel polarization and $I_{\perp}$ for perpendicular polarization) are the intensities at the peak maxima. In the perpendicular polarization distributions ($\alpha = 90^{o}$), a broad peak centered about $v_{zl} = 0$ m/s is observed. The relatively large intensities of these peaks are likely due to the fact that our apparatus tends to favor the detection of lower velocity photoions (< ~120 m/s). This is because the solid angle of detection increases as v_{zl} decreases. For example, the detector is five times more sensitive to photoions with v_{zl} = 200 m/s than photoions with v_{zl} = 500 m/s. The reasons for this will be explained in greater detail in the near future.[22]

The translational energies corresponding to the shoulders and the main velocity peaks can be calculated from

$$E_t = mv_{zl}^2/2 \qquad (4)$$

where m is the mass of the photofragment (0.1269045 kg/mol for I). Substitutions of the lab velocities into equation (4) yield for the main peaks and shoulder peaks the values of 1.7±0.1 and 4.1±0.3 kcal/mol, respectively. This corresponds to a difference of 2.4±0.3 kcal/mol in the translational energies of the different excited iodine atoms produced from the photolysis reaction which results in the formation of these atoms. From momentum and kinetic energy conservation, the kinetic energy released (T) in the photolysis leading to the observed velocity spectrum from iodocyclohexane is calculated. A summary of velocity, kinetic energy release and β values is given in Table I.

B. Assignment of the Two Velocity Peaks

Cyclohexane, C_6H_{12}, is a "floppy" molecule which is known to undergo ring conformation changes or "flips."[6,7] The conformation flips are chair-chair and chair-boat conversions. The boat conformation is less stable[6] than the chair conformation by about 7 kcal/mol due to steric and eclipsing strain. Thus the chair conformer is by far the most common configuration of cyclohexane at room temperature. Obviously, in unsubstituted cyclohexane, the chair-chair flip yields equivalent structures and hence the free energy change, ΔG^o, is zero.

When a substituent, such as an iodine atom, is substituted for a hydrogen atom, the situation becomes different in that the two chair configurations are no longer equivalent. In one conformation, the axial conformer, the iodine experiences a steric interaction with the H atoms on the 3 and 5 C atoms and is termed a 1,3-diaxial interaction. The H atoms on the 3 and 5 C atoms are equivalent so that the iodine interaction with the axial hydrogen atom on the 5 carbon atom is also termed a 1,3-diaxial interaction. In the other conformation, the equatorial conformer, the I atom does not experience any 1,3-diaxial interactions. Hence the equatorial conformer is the more stable structure. Figure 1a illustrates the axial and equatorial conformers of iodocyclohexane. The equilibrium between the two conformers therefore favors the equatorial conformer. The equilibrium constant for the ax $\rightleftharpoons$ eq equilibrium can be written as

$$K_{equil} = [\text{equatorial}]/[\text{axial}] \qquad (5)$$

Table II summarizes literature values for the free energy and equilibrium constants at different temperatures. The value for K_{equil} is in the range of 2 to 3 for iodocyclohexane at room temperature.[8-10] Thus at room temperature, ~25% of iodocyclohexane is axial and ~75% is equatorial.

The observed intensities of the two peaks in figure 3 could reflect the populations of the two conformers if one assumes that the rate of interconversion between the two conformers is slower than the rate of bond breaking in the excited state. The rate constant of the conversion from the axial to the equatorial conformers of chlorocyclohexane[8] ($C_6H_{11}Cl$) at 229 K is 400 s^{-1}, i.e. the conversion time is on the millisecond timescale. It is reasonable to assume that the conversion time for iodocyclohexane is on a similar timescale. The direct dissociation of a typical C-I bond in alkyl iodides occurs on the subpicosecond timescale.[5] If indeed the mass peaks we observe are those for the iodine atoms from the two iodocyclohexane conformers, an equilibrium constant can be calculated from the ratio of the main peak intensity to that of the shoulder peak intensity. Thus an estimate for the equilibrium constant is

$$K_{equil} = [\text{equatorial}]/[\text{axial}] = I(\text{main})/I(\text{shoulder}) \qquad (6)$$

From our data we find $K_{equil} = 2.40 \pm 0.27$ which is in good agreement with the values reported in the literature.[8-10] From a van't Hoff plot of the values of K_{equil} in table II one obtains for the heat of the axial to equatorial interconversion reaction, ΔH_r^o, a value of -0.3 kcal/mol. Thus $H_f^o(e) - H_f^o(a) = -0.3$ kcal/mol, which gives for ΔS^o a value[8] of 1 cal/mol K.

From the above discussion, we assign the weaker peak in the velocity distribution spectrum in figure 3 to the axial conformer and the dominant stronger peak to the equatorial conformer. Thus the fast velocity shoulder is due to excited iodine atoms produced from the photodissociation of a-$C_6H_{11}I$ and the slow velocity main peak is due to iodine atoms from e-$C_6H_{11}I$. Therefore, axial iodine photofragments have a larger translational energy than the equatorial photofragments.

C. The Internal Energies of the Radicals Produced upon Photodissociation

From the above assignment and the results of table I, one concludes that the kinetic energy released in the photolysis of a-C_6H_{11} is larger than that produced in the photolysis of e-$C_6H_{11}I$ by 6.0±0.8 kcal/mol. From energy balance one can write

$$h\nu = D_0^e + T^e + E_T^e + E_I = D_0^a + T^a + E_T^a + E_I \qquad (7)$$

or

$$(D_0^a - D_0^e) + (T^a - T^e) + (E_T^a - E_T^e) = 0 \qquad (8)$$

where D_0, T and E_T are the dissociation energy of the C-I bond into I atoms in the $^2P_{1/2}$ state, the kinetic energy release, and the internal energy excitation of the radical photoproducts produced in the photolysis reaction with respect to the radical's zero point energy of its ground state, respectively. E_I is the electronic energy of the iodine atom with respect to its ground electronic state. The superscripts a and e refer to the axial and equatorial conformers of iodocyclohexane, respectively. Equation (8) can be changed to

$$(D_0^a - D_0^e) + 6 = E_T^e - E_T^a \qquad (9)$$

where E_T^0 is the internal energy of the radical in its ground state. The C-I bond length of a-$C_6H_{11}I$ is slightly longer than that for e-$C_6H_{11}I$ and is thus expected to be weaker by an amount x kcal/mol (x greater than zero). Thus equation (9) can be rewritten as

$$E_T^e - E_T^a = 6.0 - x \tag{10}$$

The quantity x is expected to be much less than 6.0 kcal/mol. The radical produced from a-$C_6H_{11}I$ is expected to possess excitation of the C(3)-H and C(5)-H wagging vibration due to the strong coupling of the excited electron on the iodine to these axial hydrogen atoms in a-$C_6H_{11}I$. In spite of this, the radical produced from the photolysis of e-$C_6H_{11}I$ apparently possesses more internal excitation energy than that radical produced from the photolysis of a-$C_6H_{11}I$. This can only be understood if the radical produced from the dissociation of a-$C_6H_{11}I$ is energetically near the ground state of the cyclohexyl radical. This means that the ground state of this radical is the one with the unpaired electron in the axial position or, equivalently, the hydrogen atom on this same carbon atom in the equatorial position, i.e. an equatorial radical (equatorial and axial refer to the position of I in the parent molecule, and to the position of H at the radical center in the cyclohexyl radical photoproduct, see figure 1).

Theoretical studies[20,21] have been performed on the relative stabilities of the possible structures of the cyclohexyl radical. The cyclohexyl radical probably exists in the chair conformation[20,21] with the hydrogen atom on the radical center in an equatorial or axial position. *Ab initio* calculations[20] suggest that the axial radical conformer is more stable than the equatorial radical conformer by 0.14 kcal/mol. However, a more recent MM2 calculation[21] suggests that the cyclohexyl radical exists only in the equatorial conformation and that there is no stable axial radical conformer. This means that upon photodissociation both a-$C_6H_{11}I$ and e-$C_6H_{11}I$ give the same radical products, but with different amounts of internal excitation due to the different degrees of structural change during the photodissociation. This prediction is in agreement with our observations because e-$C_6H_{11}I$ will produce a radical with its structure unrelaxed relative to the equilibrium structure of the radical, thus leading to a higher amount of internal excitation than in a-$C_6H_{11}I$.

The *ab initio* calculations by Lloyd et al.[20] which suggest that the axial form of the radical is more stable than the equatorial form were performed under the assumption that the radical center retains an sp^3 geometry. However, one expects the C-C-C bond angle to open more upon the loss of a substituent and adopt a geometry which is more sp^2 in character. In fact, calculations[21] show that the C-C-C bond angle at the radical center is 118.4°. This would clearly make the radical center more planar and the hydrogen atom would have no choice but to occupy the equatorial position.

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Table I. Summary of observed velocity, kinetic energy release and β values from the photodissociation of $C_6H_{11}I$ for $\alpha = 0^o$. The errors in v_{zl} and β are standard deviations from the mean. The errors in T are determined from propagation of errors.

Iodine frament state	Wavelength (nm)	v_{zl} (m/s)	T (kcal/mol)	β
I* (main)	304.02	336±11	4.3±0.3	0.95±0.11
I* (shoulder)		522±17	10.3±0.8	1.26±0.14
I	304.67	573±11	12.5±1.3	1.42±0.08

Table II. Experimental and literature values of ΔG^{o} and K_{equil} for the axial to equatorial interconversion of the iodocyclohexane conformers.

T(K)	ΔG^{o} (kcal/mol)	K_{equil}	Reference
298	$-0.52\pm.07$	2.40 ± 0.27	This work
298	-0.61	2.80*	8
298	-0.48	2.25*	9
298	-0.58	2.66*	10
193	-0.468	3.39	12
180	-0.455	3.57*	15

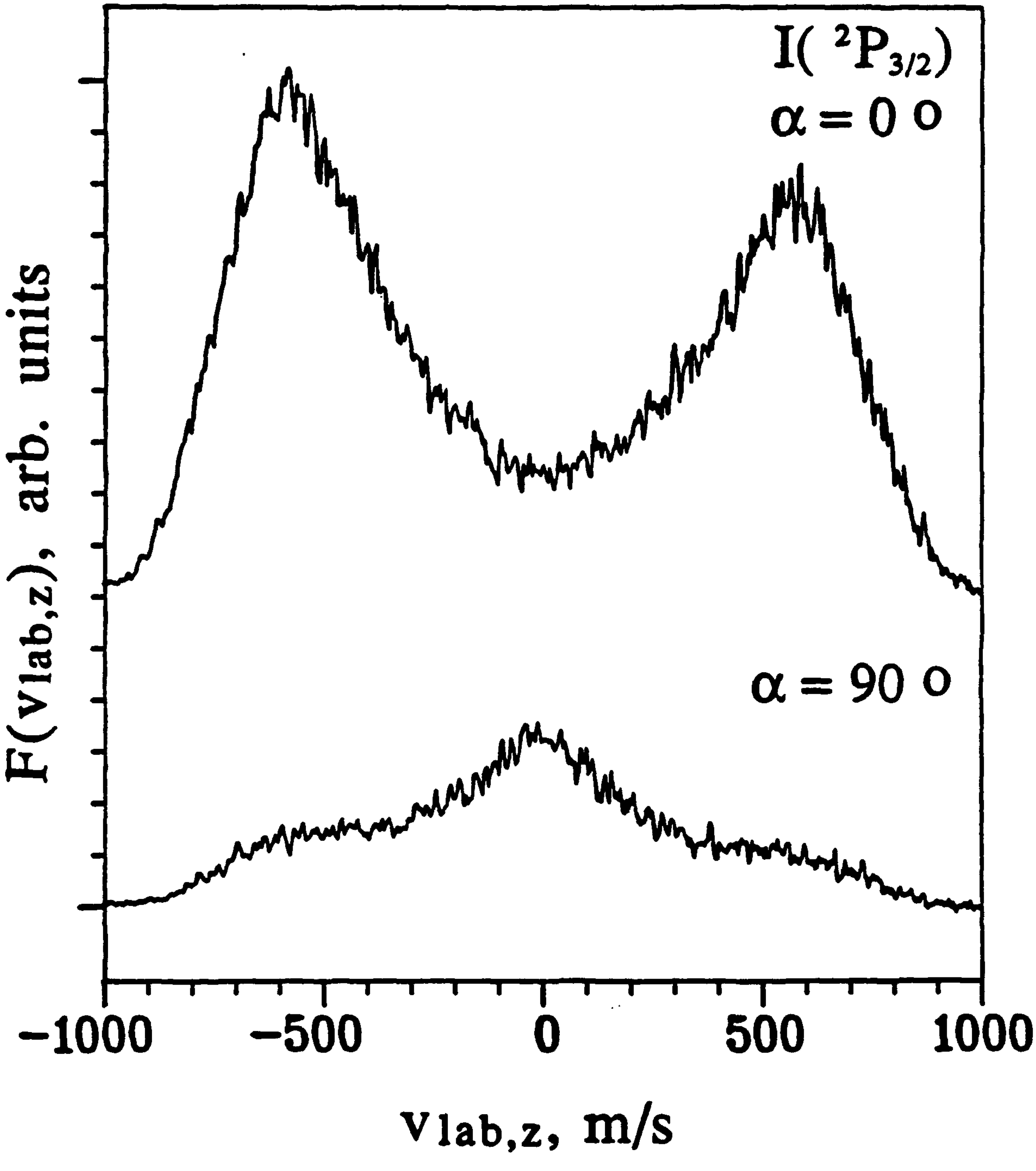
*calculated from $\Delta G^{o} = -RT\ln K_{equil}$

FIGURE CAPTIONS

Figure 1: (a) Illustration of the axial to equatorial conformation changes in iodocyclohexane. Note that the axial conformer experiences steric interaction between the iodine atom and the axial hydrogen atoms.
(b) Illustration of the axial and equatorial forms of the cyclohexyl radical. Note that the geometry of the equatorial form of the radical more closely resembles the geometry of axial iodocyclohexane than does the axial form of the cyclohexyl radical.

Figure 2: Laboratory velocity distributions of the ground state iodine photofragment (304.67 nm, 25 μJ/pulse). The upper velocity distribution trace is from laser light polarized parallel to the detection axis ($\alpha = 0^o$). The lower velocity distribution trace is from laser light polarized perpendicular to the detection axis ($\alpha = 90^o$).

Figure 3: Laboratory velocity distributions of the excited state iodine photofragment (304.02 nm, 50 μJ/pulse). The upper velocity trace is from laser light polarized parallel to the detection axis ($\alpha = 0^o$). The lower velocity distribution trace is from laser light polarized perpendicular to the detection axis ($\alpha = 90^o$). The fast velocity shoulders, which are assigned to the axial conformer of $C_6H_{11}I$, are labelled a; the dominant slower velocity main peaks, which are assigned to the equatorial conformer of $C_6H_{11}I$, are labelled e.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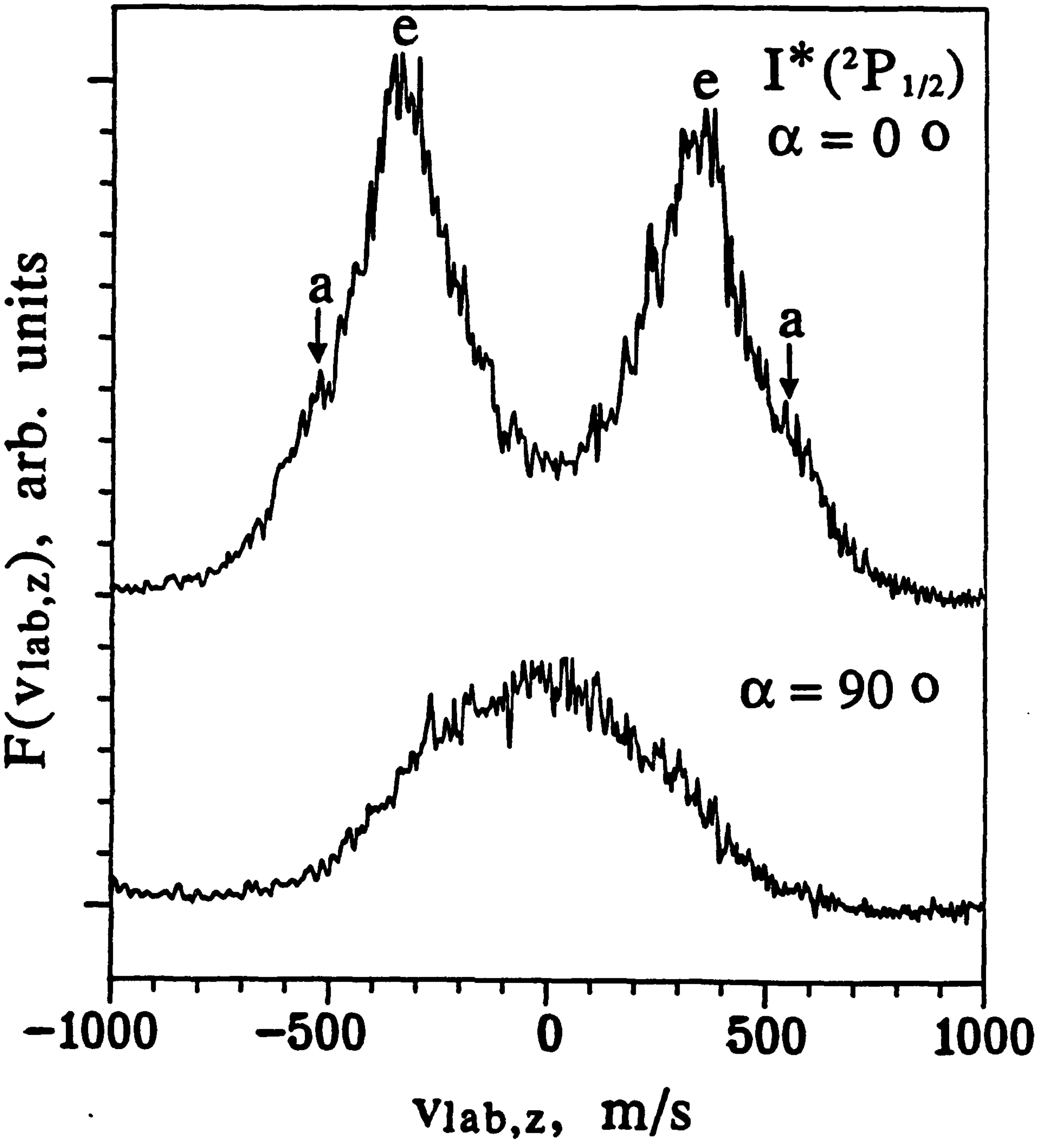
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