Infrared spectrum of the I\(^-\)–D\(_2\) anion complex

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The infrared spectrum of the I\(^-\)–D\(_2\) anion complex is measured in the D\(_2\) stretch region by monitoring production of I\(^-\) photofragments. The rotationally resolved spectrum consists of two overlapping \(\Sigma\Sigma\) subbands, redshifted by \(\approx 58 \text{ cm}^{-1}\) from the free D\(_2\) fundamental vibrational band. These subbands are associated with absorptions by I\(^-\)–D\(_2\) complexes containing \emph{ortho} and \emph{para} forms of D\(_2\). The measured rotational constants are consistent with a 3.79 Å separation between I\(^-\) and the D\(_2\) center of mass, contracting by 0.08 Å when the D\(_2\) subunit is vibrationally excited. Spectroscopic data are used to generate effective radial potential energy curves describing the interaction of \emph{ortho} and \emph{para} D\(_2\) with I\(^-\) from which the dissociation energies of I\(^-\)–D\(_2\)\(_{\text{ortho}}\) and I\(^-\)–D\(_2\)\(_{\text{para}}\) are estimated as \(D_0=236\) and 297 cm\(^{-1}\), respectively. © 2004 American Institute of Physics. [DOI: 10.1063/1.1822920]

I. INTRODUCTION

High-resolution spectra of weakly bound complexes and clusters provide valuable data for developing and assessing intermolecular potential energy surfaces.\(^1\)–\(^3\) Although the majority of spectroscopic investigations have focussed on neutral van der Waals complexes, in recent years high-resolution spectra have also been obtained for charged species.\(^4\) Anion complexes have proved particularly challenging targets and currently the only fully rotationally resolved IR spectra are for the halide-H\(_2\) dimers (Cl\(^-\)–H\(_2\), Cl\(^-\)–D\(_2\), Cl\(^-\)–HD, Br\(^-\)–H\(_2\), Br\(^-\)–D\(_2\), and I\(^-\)–H\(_2\); Refs. 5–9). The present study of I\(^-\)–D\(_2\) continues and complements earlier work.

Spectroscopic and theoretical studies have shown that the H\(_2\) molecule tends to establish a linear hydrogen bond with halide anions.\(^5\)–\(^8\),\(^10\) While the integrity of the H\(_2\) subunit is largely maintained in the complex, formation of the H bond is accompanied by marginal proton transfer towards the halide, which is manifested in a redshift of the H–H stretching frequency. The extent of the proton transfer, magnitude of the redshift, and dissociation energy of the complexes all track the proton affinity of the halide anion, decreasing in the order F\(^-\) > Cl\(^-\) > Br\(^-\) > I\(^-\).

Due to the low masses and large rotational constants of the H\(_2\) and D\(_2\) molecules, the halide-H\(_2\) and halide-D\(_2\) complexes are floppy and zero-point excitations are substantial. Tunnelling between equivalent linear minima through a \(T\)-shaped transition state plays a particularly significant role. Experimentally, the consequences of this tunnelling have been observed in the D–D stretch bands of Cl\(^-\)–D\(_2\) and Br\(^-\)–D\(_2\) through a doubling of each rovibrational line (separation \(\approx 0.24 \text{ cm}^{-1}\) for Cl\(^-\)–D\(_2\) and 0.57 cm\(^{-1}\) for Br\(^-\)–D\(_2\)). The lines’ separation is related to the difference in the tunnelling splittings for X\(^-\)–D\(_2\) complexes governed by the effective X\(^-\) + D\(_2\)(\(v_\text{DD}=0\)) and X\(^-\) + D\(_2\)(\(v_\text{DD}=1\)) potential energy surfaces. Due to the larger ionic radius of I\(^-\), one might anticipate that the intermolecular bond in I\(^-\)–D\(_2\) is longer and weaker than it is in Cl\(^-\)–D\(_2\) and Br\(^-\)–D\(_2\) and that the tunnelling splittings will be larger.

The spectroscopic data for I\(^-\)–D\(_2\) presented in this paper together with information previously gathered for I\(^-\)–H\(_2\) should in the future prove useful for testing \emph{ab initio} potential energy surfaces describing the I\(^-\) + H\(_2\) interaction and, more generally, for assessing the efficacy of different \emph{ab initio} approaches for dealing with heavier anions.

II. EXPERIMENTAL METHODS

Details of the experimental arrangement can be found in Refs. 5 and 11. Briefly, the infrared spectrum of I\(^-\)–D\(_2\) was obtained by monitoring production of I\(^-\) photofragments as the IR wavelength was scanned over the D–D stretch region. The experimental setup is essentially a home-built tandem mass spectrometer equipped with an ion source designed to generate cooled cluster ions. The mass spectrometer consists of a primary quadrupole mass filter for selection of I\(^-\)–D\(_2\) ions, an octopole ion guide where the ions are overlapped with the counterpropagating output of a pulsed tunable IR OPO (Continuum Mirage 3000 OPO, \(\approx 0.017 \text{ cm}^{-1}\) bandwidth), and a second quadrupole mass filter tuned to the mass of the daughter I\(^-\) ions. The I\(^-\)–photofragments were sensed with a channel plate detector. Wavelength calibration was accomplished using a wave meter (New Focus 7711) to measure the wavelength of the signal output from the first stage of the optical parametric oscillator, and the 532 nm output of the seeded Nd YAG laser. Line wave numbers were corrected by \(+0.04 \text{ cm}^{-1}\) to account for the Doppler shift arising from the ions’ 10 eV kinetic energy in the octopole ion guide where they interacted with the IR beam.

The I\(^-\)–D\(_2\) complexes were produced in an electron beam crossed supersonic expansion of Ar seeded with 5% D\(_2\) and traces of CH\(_3\)I as a source of I\(^-\). Optimum complex formation required relatively small separation between the
III. RESULTS AND ANALYSIS

The infrared spectrum of $\Gamma - D_2$ in the D–D stretch region (2925–2947 cm$^{-1}$ range) is displayed in Fig. 1. The D–D stretch band is redshifted by $\approx$58 cm$^{-1}$ from the transition of the free D$_2$ molecule. The relative shift of the band ($\Delta \nu / \nu_{\text{DD}} = 0.019$) is very similar to that of $\Gamma - H_2$ ($\Delta \nu / \nu_{\text{RH}} = 0.018$). The spectrum comprises two overlapping $\Sigma - \Sigma$ subbands that are associated with complexes containing para and ortho D$_2$ (see inset to Fig. 1). Altogether 25 lines were assigned to $\Gamma - D_2(o)$ and 27 lines to $\Gamma - D_2(p)$. Line wave numbers for the two bands were separately fitted using a linear pseudodiatomic transition energy expression,

$$\nu_{\text{obs}} = \nu_s + B'\left[ J^\prime(J^\prime + 1) \right] - D'\left[ J^\prime(J^\prime + 1) \right]^2 \tag{1} - B''\left[ J''(J'' + 1) \right] + D''\left[ J''(J'' + 1) \right]^2.$$ 

The fitted spectroscopic constants are listed in Table I. The origin of the $\Gamma - D_2(o)$ band lies 1.45 cm$^{-1}$ to higher energy from that of $\Gamma - D_2(p)$, but aside from this the spectroscopic constants for the two forms are the same within experimental error.

One can conclude that $\Gamma - D_2$ essentially consists of an $\Gamma^-$ anion weakly attached to a D$_2$ molecule firstly because the D–D vibrational transition of $\Gamma - D_2$ is only slightly shifted from that of D$_2$, and second because the only observed photofragment is $\Gamma^-$.

IV. EMPIRICAL INTERMOLECULAR RADIAL POTENTIALS

The rotational and centrifugal distortion constants were used as ingredients to develop four radial intermolecular potential energy curves describing the interactions of $\Gamma^-$ with D$_2$ (para, $v_{\text{DD}} = 0$), D$_2$ (para, $v_{\text{DD}} = 0$), D$_2$ (ortho, $v_{\text{DD}} = 1$), and D$_2$ (ortho, $v_{\text{DD}} = 1$).
and D2\(^{(para,v_{DD}=1)}\)). The procedure for generating the potentials is fully described in earlier publications.\(^6,8\) Briefly, the rotational and centrifugal distortion constants are used as inputs for a rotational RKR procedure\(^14,15\) to define a Morse potential appropriate for the effective radial potential near the minimum,

\[
V_M(R) = a_o + D_\chi(e^{-2\beta(x-1)} - 2e^{-\beta(x-1)}),
\]

where \(x = R/R_e\).

At longer ranges the effective radial potential is defined by solving the hindered rotor Hamiltonian at a series of fixed intermolecular separations. This assumes that the radial vibrational motion is governed by an effective potential defined by averaging over the faster bending/hindered rotation motion in what amounts to a Born-Oppenheimer (BO) separation. The angular dependence of the intermolecular interaction is obtained by considering the charge-quadrupole and induction interactions between the halide and the D\(_2\) molecule. Vibrationally averaged quadrupole moments and polarizabilities for D\(_2\) are taken from Ref. 16. At each separation the lowest energy solution is allied with a wave function that is symmetric with respect to exchange of the two D atoms and is associated with \(\Gamma^-\) interacting with \(\text{ortho} \ D_2\). The antisymmetric state lies higher in energy and is associated with \(\Gamma^-\) interacting with \(\text{para} \ D_2\). The lowest eigenvalues of the hindered rotor Hamiltonian are subsequently fitted to an inverse power series in \(R\),

\[
V_{BO}^{\text{IR}}(R) = a_0 - \frac{a_3}{R^3} - \frac{a_4}{R^4} - \frac{a_5}{R^5},
\]

where \(a_0\) corresponds to the energy of the dissociation limit. For \(\Gamma^-\) + \(D_2\)\(^{(ortho)}\) the dissociation limit corresponds to \(\Gamma^-\) + \(D_2\)\((j = 0)\) so that \(a_0 = 0\), whereas for \(\Gamma^-\) + \(D_2\)\(^{(para)}\) the dissociation limit corresponds to \(\Gamma^-\) + \(D_2\)\((j = 1)\) so that \(a_0 = 2b_{DD}\). The Morse and long-range potentials \([V_M(R)\) and \(V_{BO}^{\text{IR}}(R)\)] are spliced to give the total potential,

\[
V_{tot}(R) = f(R)V_M(R) + g(R)V_{BO}^{\text{IR}}(R),
\]

where \(f(R)\) and \(g(R)\) are switching functions

\[
f(R) = 0.5[\tanh(w(R_j - R)) + 1]\]

\[
g(R) = 0.5[\tanh(w(R - R_j)) + 1].
\]

For all four potential energy curves, the short-range Morse potential is joined to the long-range BO potential at \(R_j = 4.25\ \text{Å}\) using the switching functions with \(w = 10\ \text{Å}^{-1}\). Parameters for the potential energy curves are provided in Table II.

The BO-RKR curves for \(\Gamma^-\) + \(D_2\)\(^{(o,v_{DD}=0)}\) and \(\Gamma^-\) + \(D_2\)\(^{(p,v_{DD}=0)}\) are plotted together in Fig. 2. Near the equilibrium separation (\(R_e = 3.72\ \text{Å}\)) the two curves are very similar, but at longer range the \(\Gamma^-\) + \(D_2\)\(^{(p,v_{DD}=0)}\) curve, which has as its asymptote the \(\Gamma^-\) + \(D_2\)\((v_{DD}=0, j = 1)\) limit, is more attractive. The \(\Gamma^-\) + \(D_2\)\(^{(o,v_{DD}=0)}\) curve is predicted to have a depth of 280 cm\(^{-1}\) (\(D_0 = 236\ \text{cm}^{-1}\)) whereas the depth of the \(\Gamma^-\) + \(D_2\)\(^{(p,v_{DD}=0)}\) curve is 345 cm\(^{-1}\) (\(D_0 = 297\ \text{cm}^{-1}\)). It is worth noting that there is a minor inconsistency in the empirical curves. The wave function for the lowest energy level of the complex is symmetric with respect to exchange of the D atoms and should be associated with the \(\Gamma^-\) + \(D_2\)\(^{(o,v_{DD}=0)}\) curve. However, the empirical \(\Gamma^-\) + \(D_2\)\(^{(p,v_{DD}=0)}\) curve is slightly deeper than the \(\Gamma^-\) + \(D_2\)\(^{(o,v_{DD}=0)}\) curve so that the ground intermolecular stretch level of the former is predicted to lie slightly lower than the latter (by \(\sim 1\ \text{cm}^{-1}\)). This inconsistency probably relates to the relatively large errors (\(\sim 20\%)\) in the measured centrifugal distortion constants that are used in the generation of the empirical potential curves.

As a second example the \(\Gamma^-\) + \(D_2\)\(^{(o,v_{DD}=0)}\) and \(\Gamma^-\) + \(D_2\)\(^{(p,v_{DD}=1)}\) potential curves are plotted in Fig. 3. The effects of vibrationally exciting the D\(_2\) subunit are clearly apparent; the \(v_{DD}=1\) curve is \(\sim 45\ \text{cm}^{-1}\) deeper than the \(v_{DD}=0\) curve and the equilibrium separation is reduced by 0.072 Å. The vibrationally mediated enhancement of the \(\Gamma^-\) + \(D_2\) intermolecular interaction is due to increases in the vibrationally averaged polarizability and quadrupole moment.
of the D₂ upon going from \(v_{DD}=0\) to \(v_{DD}=1\). The difference in \(D₀\) values for the two curves in Fig. 3 should correspond to the red shift of the D–D stretch transition of \(\Gamma – D₂\) with respect to the D–D stretch transition of the free D₂ molecule. In fact, \(D₀ – D₁ = – 43 \text{ cm}^{-1}\) around 20% less than the experimentally observed redshift (\(\approx – 58 \text{ cm}^{-1}\)).

At this stage there are no other experimental or theoretical data against which to test the \(\Gamma – D₂\) BO-RKR curves. However, it should be remarked that similar curves developed for \(\text{Cl}^– – H₂\) and \(\text{Cl}^– – D₂\) yield predictions for dissociation energies that accord well with recent \textit{ab initio} and rovibrational calculations.¹⁷,¹⁸

V. DISCUSSION

A. General

The spectroscopic data and BO-RKR potential curves provide a view of the way in which an \(\Gamma^–\) ion interacts with a D₂ molecule. Predictably the properties of the \(\Gamma – D₂\) complex are very similar to those of the previously characterized \(\Gamma – H₂\) complex, and more generally with those of the \(\text{Cl}^– – H₂\), \(\text{Cl}^– – D₂\), \(\text{Br}^– – H₂\), and \(\text{Br}^– – D₂\) systems. In each case the H–H (D–D) stretch band possesses a \(\Sigma – \Sigma\) structure demonstrating that the complexes possess linear equilibrium geometries as expected from consideration of the long-range electrostatic interaction between the halide anion and the quadrupole moment on the H₂ or D₂ molecule (attractive for a linear geometry and repulsive for a T-shaped configuration). Vibrationally averaged intermolecular separations, deduced from the rotational constants assuming an undistorted D₂ monomer, are 3.789 ± 0.006 Å for \(\Gamma – D₂(o)\) and 3.786 ± 0.006 Å for \(\Gamma – D₂(p)\). The vibrationally averaged intermolecular bond distances for \(\Gamma – D₂(o)\) and \(\Gamma – D₂(p)\) are slightly less (by 0.06 Å) than that previously determined for \(\Gamma – H₂(o)\) (3.851 Å),⁷ the difference being due to greater zero point motion in the intermolecular stretch and bend coordinates for the \(\Gamma – H₂\) system. Exciting the D₂ subunit to \(v_{DD}=1\) results in a shortening and stiffening of the intermolecular bond (\(\Delta R_{\text{NN}} = – 0.079 \text{ Å}\)). These effects, which are discernible in the \(\Gamma + D₂(v_{DD}=0)\) and \(\Gamma + D₂(v_{DD}=1)\) potential energy curves in Fig. 3, are attributable to increases in the quadrupole moment and polarizabilities of D₂ in the \(v_{DD}=1\) state.

Large amplitude tunnelling motion between equivalent linear configurations of \(\Gamma – D₂\), corresponding to exchange of the two D atoms, is manifested as a tunnelling splitting of the energy levels. The wave function associated with the lower tunnelling level is symmetric with respect to the tunnelling coordinate and correlates with \(\Gamma\) interacting with \(\text{ortho}\) D₂ (even D₂ rotational levels), while the upper level is antisymmetric and correlates with \(\Gamma\) interacting with \(\text{para}\) D₂ (odd D₂ rotational levels).¹⁹ Interconversion between symmetric (\textit{ortho}) and antisymmetric (\textit{para}) forms through radiative or collisional processes is expected to be extremely inefficient, making it convenient to consider \(\Gamma – D₂(o)\) and \(\Gamma – D₂(p)\) as distinct species. In the limit of an infinite barrier for internal rotation, the energy levels (and IR spectra) of \(\Gamma – D₂(p)\) and \(\Gamma – D₂(o)\) would coincide, while at the other extreme, for entirely unhindered internal rotation, the \textit{ortho/para} levels would be separated by \(\approx 2h_{\text{DD}}=59.8 \text{ cm}^{-1}\). In fact, the tunnelling barrier for \(\Gamma – D₂\) lies between these two extremes and depends upon the vibrational state of the D₂ subunit. As the quadrupole moment of D₂ increases by \(\approx 8\%\) when it is excited from the \(v_{DD}=0\) to the \(v_{DD}=1\) vibrational state,¹⁶ the effective tunnelling barrier should be larger in the upper state, reducing the \textit{ortho/para} splitting. For this reason, the \(\Gamma – D₂(p)\) transitions occur at lower energy (by 1.45 \text{ cm}^{-1}\) than the corresponding transitions of \(\Gamma – D₂(o)\) (Fig. 1).

The relative stabilities of \(\Gamma – D₂(o)\) and \(\Gamma – D₂(p)\) play a key role in deciding their populations in the ion source, and therefore the relative intensities of the two subbands in Fig. 1. Initially it may seem surprising that the \(\Gamma – D₂(o)\) lines are weaker than the \(\Gamma – D₂(p)\) lines (the intensity ratio is \(\approx 0.6\)), given that the \textit{ortho/para} population ratio is 2:1 for natural D₂ gas. The cause, as explained in Refs. 6 and 8 in relation to \(\text{Cl}^– – D₂\) and \(\text{Br}^– – D₂\), is that \(\Gamma – D₂(p)\) is \(\approx 2h_{\text{DD}}\) more stable than \(\Gamma – D₂(o)\) (\(D₀ = 297\) vs 235 \text{ cm}^{-1}\) and thus favored in the low temperature supersonic expansion of the ion source. Any \(\Gamma – D₂(o)\) complexes that are formed are liable to be converted to \(\Gamma – D₂(p)\) in the early part of the expansion through the exothermic \(\Gamma – D₂(o) + D₂(p)\to\Gamma – D₂(p) + D₂(o)\) ligand switching reaction.

The rotational temperatures of the \(\Gamma – D₂(o)\) and \(\Gamma – D₂(p)\) populations, estimated from intensities of the less congested R-branch lines, are both \(\approx 40\) K, similar to the temperature of \(\text{Br}^– – D₂(o)\) and \(\text{Br}^– – D₂(p)\) complexes investigated previously.⁸ If one assumes that the \(\Gamma – D₂(o) + D₂(p)\to\Gamma – D₂(p) + D₂(o)\) ligand exchange reaction is exothermic by \(2h_{\text{DD}}=60 \text{ cm}^{-1}\) and had reached equilibrium at the complexes’ effective rotational temperature, the ratio of the \(\Gamma – D₂(o)\) to \(\Gamma – D₂(p)\) populations would be roughly 0.25. This is somewhat lower than the observed population ratio of 0.6 deduced from the relative intensities of the rovibrational lines. The discrepancy perhaps indicates that the ligand exchange process in fact does not reach equilibrium in the expansion, and terminates earlier than the rotational cooling. It is worth commenting that the corresponding \(X^– – H₂(p) + H₂(o)\to X^– – H₂(o)\to H₂(p)\) (\(X = \text{Cl,Br,J}\)

<p>| TABLE III. Potential well depths (D_0), dissociation energies (D_0), and vibrational energy level spacings for the BO-RKR potential curves of (\Gamma – D₂(o)) and (\Gamma – D₂(p)). The vibrational band shift (\Delta v) is the difference in (D_0) values for the (v_{DD}=0) and (v_{DD}=1) curves. All values are in \text{cm}^{-1}. The number of bound stretching levels supported by each potential curve is also given. |</p>
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<thead>
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<th>(\Gamma – D₂(o))</th>
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<td>(E(5,0))</td>
<td>222</td>
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<td>9 levels</td>
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ligand exchange processes, which are exothermic by $2b_{\text{HH}} \approx 120 \text{ cm}^{-1}$, are so efficient that only the $X^- - \text{H}_2(o)$ species have been observed.$^{5,7}$

**B. Comparison of $\text{Cl}^- - \text{D}_2$, $\text{Br}^- - \text{D}_2$, and $\text{I}^- - \text{D}_2$**

The current study enables us to compare the properties of $\text{I}^- - \text{D}_2$ with those of $\text{Cl}^- - \text{D}_2$ and $\text{Br}^- - \text{D}_2$ whose rotationally resolved infrared spectra were reported previously.$^{6,8}$ Differences between interactions in the three systems are exemplified in Fig. 4 where effective radial BO-RKR curves for $\text{I}^- + \text{D}_2(o)$, $\text{Br}^- + \text{D}_2(o)$, and $\text{Cl}^- + \text{D}_2(o)$ are plotted together. The long-range parts of the curves, which are generated by considering the induction and electrostatic interactions are almost identical. Predictably, as the halide becomes larger, the well depth diminishes and the radial equilibrium separation increases ($R_e = 3.11 \AA$ and $D_0 = 499 \text{ cm}^{-1}$ for $\text{Cl}^- - \text{D}_2$, $R_e = 3.36 \AA$ and $D_0 = 364 \text{ cm}^{-1}$ for $\text{Br}^- - \text{D}_2$, and $R_e = 3.72 \AA$ and $D_0 = 235 \text{ cm}^{-1}$ for $\text{I}^- - \text{D}_2$). The comparatively weak intermolecular interaction for $\text{I}^- - \text{D}_2$ is reflected in the magnitude of the $\text{D}_2$ vibrational band shift ($\approx 58 \text{ cm}^{-1}$), which is smaller than those of $\text{Br}^- - \text{D}_2$ and $\text{Cl}^- - \text{D}_2$ (85 and 114 cm$^{-1}$, respectively). Perhaps surprisingly, the intermolecular bond contractions following vibrational excitation of the $\text{D}_2$ subunit are similar for $\text{I}^- - \text{D}_2$, $\text{Br}^- - \text{D}_2$, and $\text{Cl}^- - \text{D}_2$ ($\Delta R_{\text{cm}} = -0.079$, $-0.076$, and $-0.078 \AA$, respectively).

**C. Vibrational predissociation**

Widths of the $\text{I}^- - \text{D}_2$ rovibrational lines are close to the bandwidth of the OPO output ($\approx 0.017 \text{ cm}^{-1}$). Any contribution to the lines’ widths from homogeneous lifetime broadening is estimated to be less than 0.01 cm$^{-1}$, implying that vibrational predissociation proceeds on a time scale exceeding 530 ps. An upper limit for the time scale of the fragmentation process is provided by the observation that dissociation ensues during the ions’ passage through the octopole region of the apparatus ($\approx 50 \mu$s). As far as we could ascertain, there was neither a $J$ dependence for the line widths nor any difference between the predissociation rates of $\text{I}^- - \text{D}_2(o)$ and $\text{I}^- - \text{D}_2(p)$. The observations are consistent with trends deduced from earlier studies of $\text{F}^- - \text{H}_2$, $\text{Cl}^- - \text{H}_2$, $\text{Cl}^- - \text{D}_2$, $\text{Br}^- - \text{H}_2$, $\text{Br}^- - \text{D}_2$, and $\text{I}^- - \text{H}_2$. Generally, the vibrational predissociation rate diminishes as the halide becomes larger, and is also reduced when $\text{H}_2$ is replaced by $\text{D}_2$.

**VI. CONCLUSIONS**

Outcomes of the current work can be summarized as follows.

1. The D–D stretch band of $\text{I}^- - \text{D}_2$ is redshifted by $\approx 58 \text{ cm}^{-1}$ from the free $\text{D}_2$ molecule absorption and is composed of two $\Sigma - \Sigma$ subbands, separated by $1.45 \text{ cm}^{-1}$, corresponding to absorptions by $\text{I}^- - \text{D}_2$ (orth) and $\text{I}^- - \text{D}_2$ (para).

2. The $\text{I}^- - \text{D}_2$ complex possesses a linear equilibrium structure with a vibrationally averaged intermolecular separation of $3.79 \AA$.

3. Vibrational excitation of the $\text{D}_2$ subunit leads to a 0.079 Å contraction of the $\text{I}^- - \text{D}_2$ intermolecular bond.

4. Effective dissociation energies of 235 and 297 cm$^{-1}$ are deduced for $\text{I}^- - \text{D}_2$ (orth) and $\text{I}^- - \text{D}_2$ (para), respectively.

5. Linewidths are limited by the light source bandwidth (0.017 cm$^{-1}$), demonstrating that predissociation takes place on a time scale exceeding 530 ps following vibrational excitation of the $\text{D}_2$ subunit.

Developing accurate $ab$ initio surfaces describing negatively charged complexes containing the heavier halides remains a challenging enterprise. Reproduction of the rotational constants and vibrational frequencies for $\text{I}^- - \text{D}_2$ reported in this paper along with previously reported spectroscopic data for $\text{I}^- - \text{H}_2$ should serve as critical tests for three-dimensional $ab$ initio potential energy surfaces describing the $\text{I}^- + \text{H}_2$ interaction.

**ACKNOWLEDGMENTS**

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19 Even and odd $j$ levels of $D_2$ are associated respectively with the *ortho* and *para* modifications. Note that in Refs. 2 and 3 the *ortho/para* designations for $D_2$ were mistakenly reversed.