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**Rotationally resolved infrared spectrum of the Li+_D2 cation complex**

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Abstract
The infrared spectrum of mass selected Li+D2 cations is recorded in the D-D stretch region (2860-2950 cm⁻¹) in a tandem mass spectrometer by monitoring Li+ photofragments. The D-D stretch vibration of Li+D2 is shifted by -79 cm⁻¹ from that of the free D2 molecule indicating that the vibrational excitation of the D2 subunit strengthens the effective Li+-D2 intermolecular interaction. Around 100 rovibrational transitions, belonging to parallel K a=0-0, 1-1, and 2-2 subbands, are fitted to a Watson A-reduced Hamiltonian to yield effective molecular parameters. The infrared spectrum shows that the complex consists of a Li+ ion attached to a slightly perturbed D2 molecule with a T-shaped equilibrium configuration and a 2.035 Å vibrationally averaged intermolecular separation. Comparisons are made between the spectroscopic data and data obtained from rovibrational calculations using a recent three dimensional Li+-D2 potential energy surface [R. Martinazzo, G. Tantardini, E. Bodo, and F. Gianturco, J. Chem. Phys. 119, 11241 (2003)].

Keywords
complex, resolved, li, spectrum, infrared, rotationally, _d2, cation

Disciplines
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Rotationally resolved infrared spectrum of the Li$^+$–D$_2$ cation complex

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The infrared spectrum of mass selected Li$^+$–D$_2$ cations is recorded in the D–D stretch region (2860–2950 cm$^{-1}$) in a tandem mass spectrometer by monitoring Li$^+$ photofragments. The D–D stretch vibration of Li$^+$–D$_2$ is shifted by $\sim$79 cm$^{-1}$ from that of the free D$_2$ molecule indicating that the vibrational excitation of the D$_2$ subunit strengthens the effective Li$^+$⋯D$_2$ intermolecular interaction. Around 100 rovibrational transitions, belonging to parallel $K_a$=0-0, 1-1, and 2-2 subbands, are fitted to a Watson A-reduced Hamiltonian to yield effective molecular parameters. The infrared spectrum shows that the complex consists of a Li$^+$ ion attached to a slightly perturbed D$_2$ molecule with a T-shaped equilibrium configuration and a 2.035 Å vibrationally averaged intermolecular separation. Comparisons are made between the spectroscopic data and data obtained from rovibrational calculations using a recent three dimensional Li$^+$–D$_2$ potential energy surface [R. Martinazzo, G. Tantardini, E. Bodo, and F. Gianturco, J. Chem. Phys. 119, 11241 (2003)]. © 2006 American Institute of Physics. [DOI: 10.1063/1.2218334]

I. INTRODUCTION

Complexes of alkali metal cations and hydrogen molecules such as Li$^+$–H$_2$ are interesting because of their relevance to molecular hydrogen absorption at alkali cation sites in zeolites, their possible participation in astrophysical processes, and their suitability to accurate theoretical treatments. Despite their significance, there are no spectroscopic data on the alkali metal-hydrogen complexes although there have been numerous theoretical studies.

Initial experimental studies of the Li$^+$–H$_2$ system were done by Toennies and co-workers who investigated vibrationally and rotationally inelastic collisions between Li$^+$ and the H$_2$ and D$_2$ molecules.$^{1–4}$ The first direct observation of Li$^+$–H$_2$ was made by Clampitt and Jefferies who found that Li$^+$ ions solvated by up to six H$_2$ molecules were ejected when a solid H$_2$ target was irradiated by a Li$^+$ beam.$^5$ Subsequently the binding energy of H$_2$ to Li$^+$ was estimated as 6.5±4.6 kcal/mol (2275 cm$^{-1}$) through appearance potential measurements of Li$^+$–H$_2$.$^6$

Most theoretical studies of Li$^+$–H$_2$ have focused on calculating the equilibrium geometry and vibrational frequencies in the harmonic approximation with the application of increasingly sophisticated levels of $ab$ initio theory.$^{7–31}$ All existing calculations agree that the Li$^+$–H$_2$ complex has a T-shaped C$_2v$ equilibrium structure with the Li$^+$ ion loosely tethered to the H$_2$ molecule, a binding geometry favored by the electrostatic interaction between the positive charge of the Li$^+$ and the H$_2$ quadrupole moment. Several studies have focused on establishing links between the strength of the cation-H$_2$ interaction and the shift in the H$_2$ vibrational frequency.$^{23,31}$

A comprehensive understanding of the Li$^+$–H$_2$ complex

\[ \text{Li}^+ \rightarrow \text{Li}^+ + \text{H}_2 \]

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\[ \text{Li}^+ \rightarrow \text{Li}^+ + \text{H}_2 \]

\[ \text{Li}^+ \rightarrow \text{Li}^+ + \text{H}_2 \]

must account for the weak nature of the Li$^+$⋯H$_2$ interaction and the large amplitude intermolecular motions which are probably poorly described by the harmonic approximation. The first effort in this direction was by Searles and Von Nagy-Felsobuki who fitted 170 $ab$ initio energy points for the Li$^+$–H$_2$ with a Padé-approximant function with a Dunham expansion variable.$^{20}$ Subsequently, Røeggen et al. calculated a Li$^+$⋯H$_2$ interaction potential for fixed H$_2$ bond length that was used in scattering calculations to model the mobility of Li$^+$ ions in H$_2$ gas.$^{29}$ More recently, Bulvchev et al. calculated a three-dimensional (3D) potential energy surface (PES) at the MP2 level and used it to determine variationally the energies for the $J=0$ rovibrational states of Li$^+$–H$_2$, Li$^+$–D$_2$, and Li$^+$–T$_2$.\(^3\)

In a comprehensive theoretical study of the Li$^+$–H$_2$ system, Martinazzo, Tantardini, Bodo, and Gianturco (MTBG) calculated a three-dimensional potential energy surface primarily to understand the astrophysically important LiH$^+$$+$$+$$H$ $\rightarrow$ Li$^+$+H$_2$ and LiH$^+$$+$$H$ $\rightarrow$ Li$^+$+H$_2$ reactions.\(^3\) The energy points, determined with complete active self-consistent field reference functions and a large Li basis set, were fitted to a functional form that accounts for the important long-range contributions to the interactions. The MTBG surface possesses a shallow well in a T-shaped C$_2v$ geometry with a Li$^+$⋯H$_2$ separation of 1.92 Å and a depth of 0.286 eV (2309 cm$^{-1}$) with respect to the Li$^+$–H$_2$ asymptote. As shown in Fig. 1 there is an appreciable 1680 cm$^{-1}$ barrier to H$_2$ internal rotation in the linear configuration. The MTBG PES was subsequently used in variational calculations to determine the $J=0$ rovibrational states of the Li$^+$–H$_2$ complex.$^{33}$

In this work we report an infrared photodissociation spectrum of Li$^+$–D$_2$ in the D–D stretch region. The spectrum, which features full rotational resolution, provides critical information to test and refine potential energy surface for the Li$^+$⋯H$_2$ interaction.
II. EXPERIMENTAL METHODS

The infrared spectrum of $^7\text{Li}^+ – \text{D}_2$ was measured by scanning the IR wavelength over the D–D stretch region while monitoring production of Li$^+$ photofragments. Vibrational energy originally localized in the D–D stretch coordinate, migrates into the weak intermolecular bond, leading to its rupture and the liberation of Li$^+$ photofragments.

The Li$^+ – \text{D}_2$ complexes were generated in a supersonic expansion of D$_2$ (stagnation pressure of 6 bars) passing over a rotating metal alloy rod (10% Li/90% Al). The rotating rod was irradiated with the fundamental (1064 nm, 7 mJ/pulse), doubled (532 nm, 3 mJ/pulse), and quadrupled (266 nm, 1 mJ/pulse) output of a pulsed Nd:YAG (yttrium aluminum garnet) laser (20 Hz repetition rate).

The tandem mass spectrometer apparatus, which has been described previously, comprises a primary quadrupole mass filter for the selection of the parent $^7\text{Li}^+ – \text{D}_2$ ions, an octopole ion guide, where the ions are overlapped with the counterpropagating output of a pulsed, tuneable IR radiation source [Continuum Mirage 3000 optical parametric oscillator (OPO) 0.017 cm$^{-1}$ bandwidth], and a second quadrupole mass filter tuned to the mass of Li$^+$ fragment ions. Photofragments were sensed with a microchannel plate coupled to a scintillator and photomultiplier tube.

Wavelength calibration was accomplished using a wavemeter (HighFinesse WS/7) 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. The transition wave numbers were corrected to account for the Doppler shift resulting from the ions’ 10 eV translational energy in the octopole ion guide. The absolute uncertainty of the line wave numbers is decided by the uncertainty of the ions’ energy in the octopole ion guide and is estimated as 0.10 cm$^{-1}$. The relative uncertainties of the lines’ wave numbers are estimated as 0.015 cm$^{-1}$. The lines’ intensities are not normalized for laser power or parent ion signal intensity which exhibits considerable shot-to-shot and longer term fluctuations.

III. RESULTS AND DISCUSSION

A. Infrared spectrum of Li$^+ – \text{D}_2$

The Li$^+ – \text{D}_2$ complex is expected to have a T-shaped equilibrium geometry favored by the electrostatic interaction between the Li$^+$ cation and the quadrupole moment of the D$_2$ molecule (see Fig. 1). The minimum energy geometry on the MTBG potential energy surface is a T-shaped structure with D–D separation of 0.751 Å and intermolecular separation of 1.916 Å. This structure corresponds to rotational constants $A=29.7$ cm$^{-1}$, $B=1.79$ cm$^{-1}$, and $C=1.69$ cm$^{-1}$ and asymmetry parameter $κ=-0.993$. Because the barrier to internal rotation of the D$_2$ subunit (1680 cm$^{-1}$) is much larger than the D$_2$ rotational constant ($b_{DD} \sim 30$ cm$^{-1}$), the internal rotation is largely quenched and the system should approach the near prolate asymmetric top limit. Therefore, the quantum number associated with the projection of the total angular momentum onto the intermolecular axis ($K_a$) is nearly good.

Even and odd $K_a$ states correspond, respectively, to Li$^+$ attached to the ortho and para modifications of D$_2$. For normal D$_2$ gas the ortho (even) and para (odd) forms occur in 2:1 ratio. Direct collisional relaxation between the two forms should be extremely inefficient in the supersonic expansion, although the exchange of D$_2$ ligands attached to the Li$^+$ is probably a facile process. Because the transition moment for excitation of the D–D stretch lies along the intermolecular bond (i.e., a parallel transition), the IR spectrum should consist of overlapping $K_a=0$-0, 1-1, 2-2, etc., subbands.

As expected from the considerations outlined above, the experimental Li$^+ – \text{D}_2$ spectrum shown in Fig. 2 has the appearance of a parallel transition of a near prolate asymmetric rotor with $K_a=0$-0, $K_a=1$-1, and $K_a=2$-2 subbands. An expanded view of the central part of the spectrum is shown in Fig. 3 where the $Q$ branches of the $K_a=1$-1, $K_a=2$-2, and $K_a=3$-3 subbands are clearly apparent. The $K_a=1$-1 $Q$...
TABLE I. Constants in cm$^{-1}$ for Li$^+$–D$_2$ obtained by fitting the D–D stretch band transitions to a Watson A-reduced Hamiltonian. Errors in the last significant figure are given in brackets.

<table>
<thead>
<tr>
<th>$\tilde{K}_{\sigma}$</th>
<th>$K_{\sigma}=0$</th>
<th>$K_{\sigma}=1$</th>
<th>$K_{\sigma}=2$</th>
<th>$K_{\sigma}=0, 1, 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B^\prime$</td>
<td>1.5960(8)</td>
<td>1.5986(6)</td>
<td>1.5986(6)</td>
<td>1.5986(6)</td>
</tr>
<tr>
<td>$C^\prime$</td>
<td>1.4971(9)</td>
<td>1.4971(9)</td>
<td>1.4971(9)</td>
<td>1.4971(9)</td>
</tr>
<tr>
<td>$\tilde{B}^\prime$</td>
<td>1.5496(6)</td>
<td>1.5466(9)</td>
<td>1.5406(30)</td>
<td>1.5493(6)</td>
</tr>
<tr>
<td>$D^\prime_J \times 10^4$</td>
<td>1.271(20)</td>
<td>1.119(55)</td>
<td>1.171(16)</td>
<td>1.163(17)</td>
</tr>
<tr>
<td>$D^\prime_R \times 10^3$</td>
<td>-2.27(16)</td>
<td>1.5935(6)</td>
<td>1.5935(6)</td>
<td>1.5935(6)</td>
</tr>
<tr>
<td>$B^\prime$</td>
<td>1.5913(7)</td>
<td>1.5913(7)</td>
<td>1.5913(7)</td>
<td>1.5913(7)</td>
</tr>
<tr>
<td>$C^\prime$</td>
<td>1.4909(8)</td>
<td>1.4909(8)</td>
<td>1.4909(8)</td>
<td>1.4909(8)</td>
</tr>
<tr>
<td>$\tilde{B}^\prime$</td>
<td>1.5438(5)</td>
<td>1.5411(8)</td>
<td>1.5358(23)</td>
<td>1.5435(6)</td>
</tr>
<tr>
<td>$D^\prime_J \times 10^4$</td>
<td>1.246(16)</td>
<td>1.111(40)</td>
<td>1.15(10)</td>
<td>1.125(14)</td>
</tr>
<tr>
<td>$D^\prime_R \times 10^3$</td>
<td>-2.10(14)</td>
<td>1.5466(5)</td>
<td>1.5466(5)</td>
<td>1.5466(5)</td>
</tr>
<tr>
<td>$\Delta \tilde{A}^\prime$</td>
<td>-0.258(3)</td>
<td>2914.623(7)</td>
<td>2913.359(6)</td>
<td>2909.586(14)</td>
</tr>
<tr>
<td>$\Delta \tilde{J}$</td>
<td>2914.620(5)</td>
<td>6.0</td>
<td>7.7</td>
<td>4.1</td>
</tr>
<tr>
<td>$\Delta \tilde{B}$</td>
<td>1.6278</td>
<td>1.6266</td>
<td>1.6205</td>
<td>1.6073</td>
</tr>
<tr>
<td>$r_{\text{ms}} \times 10^3$</td>
<td>1.22</td>
<td>1.12</td>
<td>1.04</td>
<td>1.04</td>
</tr>
</tbody>
</table>

$^a\Delta = A^\prime - A^\prime$ is the value of $A^\prime$ was fixed to 29.907 cm$^{-1}$.

$^b$Subband origins are given for $K_{\sigma}=0$, $K_{\sigma}=1$, and $K_{\sigma}=2$ subbands.

branch exhibits several resolved transitions, whereas the $K_{\sigma}=2$ and $K_{\sigma}=3$ $Q$ branches appear as single peaks with maxima at 2909.58 and 2903.45 cm$^{-1}$, respectively. Also obvious is the band gap between the $P$ and $R$ branches of the $K_{\sigma}=0$ subband and the asymmetry doubling in the $P$ and $R$ branch transitions of the $K_{\sigma}=1$ subband. The asymmetry doubling is not resolved for the $K_{\sigma}=2$ subband. Altogether, 30 lines were identified for the $K_{\sigma}=0$ subband, 45 lines in the $P$ and $R$ branches and 7 lines in the $Q$ branch of the $K_{\sigma}=1$ subband, and 14 lines in the $P$ and $R$ branches of the $K_{\sigma}=2$ subband. The transitions’ wave numbers along with assignments in terms of a semigrid asymmetric rotor model (Sec. III B) are available as supplementary material.

### B. Asymmetric rotor analysis

The transition wave numbers for the $K_{\sigma}=0$, 1, and 2 sub-band lines were fitted to an $A$-reduced Watson Hamiltonian, including $D_J$ and $D_{JR}$ distortion terms. The value of $A''$ was fixed to 29.907 cm$^{-1}$, corresponding to the $B$ rotational constant of the free D$_2$ molecule. The fit of the parallel transition determines $\Delta \tilde{A}=A^\prime-A^\prime$ but is relatively insensitive to $A'$ and $A''$ themselves. Each of the $K_{\sigma}=0$, 1, and 1, and 2-2 subbands was also fitted separately. Resulting parameters are listed in Table I. Differences between experimental transition frequencies and those calculated using the fitted parameters are included with the supplementary material.

Generally, the spectroscopic constants are compatible with expectations based on previous ab initio calculations. For example, the ground and excited state vibrationally averaged Li$^+$···H$_2$ separations estimated from $\tilde{B}''$ and $\tilde{B}'$ are 2.035 and 2.038 Å, respectively, which are comparable with equilibrium separations determined in ab initio calculations. For example, recent MP2/aug-cc-pVQZ calculations give an equilibrium Li$^+$···H$_2$ intermolecular separation of 2.01 Å.

Consideration of the spectroscopic data in Table I suggests that even in the ground vibrational state Li$^+$–D$_2$ undergoes large amplitude vibrational excursions, particularly in the bending/hindered internal rotation coordinate. For a rigid planar molecule the inertial defect $\Delta=1/C−1/B−1/A$ should be zero. Taking the experimental values for $B''$ and $C''$ (Table I) one finds $A''=24.3$ cm$^{-1}$, corresponding to a vibrationally averaged D–D separation of 0.83 Å. This represents a large increase (by 0.08 Å) in the D–D bond length from the free D$_2$ molecule value ($<r>=0.75$ Å), which is unlikely to be caused by the relatively weak interaction with the Li$^+$ ion. Indeed, the equilibrium D–D separation on the MTBG surface is 0.751 Å. The alternative to a large distortion of the D$_2$ subunit is that the effective molecular parameters are influenced by the large amplitude bending/hindered rotation of the D$_2$ subunit. As pointed out by Nesbitt and co-workers, the unquenched hindered internal rotation tends to exaggerate the asymmetry doubling and consequently $B−C$, leading to a nonzero inertial defect. The effect increases as the hindering barrier decreases.

### C. Comparison with calculated energy levels

Rovibrational calculations were undertaken using the MTBG surface to derive further insights into the Li$^+$–D$_2$ system. Energies of the lower rovibrational levels of $^7$Li$^+$–D$_2$ were calculated variationally employing the TRIATOM program with a basis set comprising 20 Morse functions in the D–D stretch, 18 Morse functions in the intermolecular stretch, and 14 Legendre functions for the angular coordinate. The masses of the Li and D atoms were taken to be 7.016 and 2.014 amu, respectively.

Energies for the lowest $J=0$–4 rovibrational levels, converged to $<10^{-3}$ cm$^{-1}$, are listed in Table II. To facilitate comparisons with the experimental data, energies for the $K_{\sigma}=0$, 1, and 2 manifolds were fitted independently to a polynomial in $J(J+1)$. Results from these fits are also given in Table II. Even and odd $K_{\sigma}$ levels correspond to Li$^+$ interacting with ortho or para D$_2$, respectively. The ground state ($J_{\text{PD}}=0, v_0=0, v_0=0, J=0$) state of Li$^+$–D$_2$ lies 1858 cm$^{-1}$ below the Li$^+$+D$_2$($J_{\text{PD}}=0, J=0$) asymptote. Due to its lower
TABLE III. Data relating to asymmetry splittings in the $K_x=1$ manifolds (units are cm$^{-1}$).

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\Delta'(J)_{\text{calc}}$</th>
<th>$\Delta'(J)_{\text{expt}}$</th>
<th>$\Delta''(J)_{\text{calc}}^a$</th>
<th>$\Delta''(J)_{\text{expt}}^a$</th>
<th>$\Delta''(J)_{\text{calc}}^b$</th>
<th>$\Delta''(J)_{\text{expt}}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.110</td>
<td>0.098</td>
<td>0.441</td>
<td>0.400</td>
<td>0.410</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.331</td>
<td>0.307</td>
<td>0.992</td>
<td>0.923</td>
<td>0.916</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.661</td>
<td>0.613</td>
<td>1.761</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a\Delta'(J)=\frac{1}{2}[(\Delta'(J)+\Delta'(J)).$

$^b\Delta''(J)=\Delta'(J)+\Delta'(J+1)$.

$^c\Delta''(J)=\Delta'(J)+\Delta'(J+1)$.

The experimental $\tilde{B}''$ value is around 5% less than the corresponding calculated value (Tables I and II), implying that the MTBG surface slightly underestimates the vibrationally averaged $\text{Li}^+\cdots\text{D}_2$ bond length. The vibrationally averaged separation $\langle\tilde{R}(\bar{J})\rangle$ estimated from the experimental $\tilde{B}''$ value (2.035 Å) is 0.056 Å longer than the value determined from the $\tilde{B}$ found from the rovibrational calculations (1.979 Å). In contrast, the vibrationally averaged intermolecular separation calculated by Bulychev et al. $\langle\tilde{R}(\bar{J})\rangle=2.051$ Å is closer to the experimental value, overestimating it by 0.016 Å.

As mentioned in Sec. III B the asymmetry splittings are sensitive to details of the $\text{Li}^+\cdots\text{D}_2$ PES, increasing as the hindering barrier for $\text{D}_2$ internal rotation decreases and also as the intermolecular bond length shortens. For this reason it would be interesting to compare experimental and calculated $\Delta''(J)$ directly from the infrared spectrum. However, from combination differences one can ascertain $\Delta''(J)\neq\Delta'(J)+\Delta'(J+1)$, $\Delta'(J)=\Delta'(J)+\Delta'(J+1)$, and $\Delta(J)=\frac{1}{2}[(\Delta''(J)+\Delta'(J)+\Delta'(J)]$. The experimental and calculated data are compiled in Table III. Firstly, it is interesting to note that the experimental $\Delta''(J)$ and $\Delta'(J)$ values are very similar, confirming that the vibrational excitation of the D$_2$ subunit has little effect on the molecular geometry or the effective tunneling barrier. Comparisons of $\Delta''(J)_{\text{calc}}$ and $\Delta''(J)_{\text{expt}}$ indicate that the calculated splittings slightly exceed the experimental splittings. At this stage it is uncertain whether the primary cause for the discrepancy is the MTBG surface’s underestimation of the $\text{Li}^+\cdots\text{D}_2$ intermolecular separation or underestimation of the effective tunneling barrier.

D. Intermolecular modes

Rovibrational calculations using the MTBG surface give frequencies of $v_5=365$ cm$^{-1}$ for the intermolecular stretch and $v_6=503$ cm$^{-1}$ for the intermolecular bend. Corresponding values calculated by Bulychev et al. are $v_5=329.8$ cm$^{-1}$ and $v_6=447.2$ cm$^{-1}$. $^{30}$ The calculated intermolecular stretch frequencies correspond reasonably well to rough estimates for the harmonic frequencies made using the $\tilde{B}$ and $D_2$ values ($\omega''_s=347$ cm$^{-1}$ and $\omega'_s=351$ cm$^{-1}$). In future it may be possible to measure the $v_{DD}+v_5$ and $v_{DD}+v_6$ combination bands providing direct information on the intermolecular modes.

E. Ground/excited state changes and vibrational redshift

The IR spectrum provides information on the dependence of the $\text{Li}^+\cdots\text{D}_2$ intermolecular interaction on the vibrational state of the $\text{D}_2$ molecule. Because the high frequency D–D stretch vibration is effectively adiabatically decoupled from the lower frequency intermolecular stretching and bending motions, one can consider the ground and excited states of the system as consisting of a $\text{Li}^+$ ion interacting with a $\text{D}_2$ molecule in the $v_{DD}=0$ and $v_{DD}=1$ states. From this perspective the effective $\text{Li}^+\cdots\text{D}_2(v_{DD}=1)$ potential surface is deeper than the $\text{Li}^+\cdots\text{D}_2(v_{DD}=0)$ potential surface by around 79.0 cm$^{-1}$ [the redshift of the $v_{DD}=1 \leftrightarrow v_{DD}=0$ transition of $\text{Li}^+\cdots\text{D}_2$ from the $Q(0)$ transition of the free $\text{D}_2$ molecule at 2993.6 cm$^{-1}$; Ref. 36].

The observed redshift is close to the shifts calculated by Bulychev et al. (77.1 cm$^{-1}$) in their 3D anharmonic vibrational calculations$^{30}$ and by Bishop and Cybulski (80.1 cm$^{-1}$), who estimated the frequency shift by solving the one-dimensional Schrödinger equation for the $\text{D}_2$ molecule perturbed by the attached $\text{Li}^+$.$^{33}$

The redshift and enhancement of the intermolecular bond strength, which have been observed in other ion complexes containing $\text{H}_2$ and $\text{D}_2$, including $\text{H}_2–\text{HCO}^+$(Ref. 40) and $\text{C}_2–\text{H}_2$, can be seen as resulting from increases in the vibrationally averaged quadrupole moment and polarizability of $\text{D}_2$ of 5%–8% going from $v_{DD}=0$ to $v_{DD}=1$, enhancing the charge-quadrupole electrostatic and charge-induced dipole induction intermolecular interactions.

Surprisingly the A, B, and C rotational constants obtained from the semirigid rotor analysis decrease when the $\text{D}_2$ subunit is vibrationally excited, demonstrating that, notwithstanding the 79 cm$^{-1}$ increase in the effective interaction energy, there is a slight increase in the vibrationally averaged intermolecular separation. The decrease in A is expected since the rotational constant of the free $\text{D}_2$ molecule decreases by 1.06 cm$^{-1}$ going from $v_{DD}=0$ to $v_{DD}=1$.$^{36}$ Decreases in the B and C constants are more surprising. We note that Bulychev et al. predicted a similar effect, finding that the vibrationally averaged intermolecular separation increased by 0.004 Å when the D–D stretch is excited.$^{30}$ The form of the MTBG surface is also consistent with the vibrationally induced increase in the intermolecular separation. As can be seen in Fig. 4 where the equilibrium $\text{Li}^+\cdots\text{D}_2$ intermolecular separation is plotted as a function of the D–D separation, there is a highly nonlinear dependence of the equilibrium intermolecular bond length on the D–D bond separation so that averaging over the D–D vibrational stretch wave function will lead to a larger mean intermolecular separation for the $v_{DD}=1$ state than for the $v_{DD}=0$ state.

F. Vibrational predissociation dynamics of $\text{Li}^+–\text{D}_2$

The observed transitions access quasibound levels that are coupled to the $\text{Li}^+\cdots\text{D}_2(v_{DD}=0)$ continuum. Widths of the individual rovibrational lines provide information on the vibrational predissociation rate. It is easiest to estimate the widths of the $K_x=0$–0 lines since they are the most intense. Fitting the lines with a Voigt profile with the full width at
I$^-$–D$_2$ anion complexes. Nevertheless, it is interesting to apparently independent of $J$ that using the same IR light source and tandem mass spectrometry, where they overlap with IR radiation. It should be remarked the ions having a spread of energy in the octopole region lines may be power broadened or Doppler broadened due to note that Sanz et al. (Ref. 32) upper state lifetime of D–D separation.

The highly nonlinear dependence of the intermolecular separation on the dimension of the D–D stretch energy levels and associated wave functions. Note the Li$^+$–D$_2$ complex has a T-shaped equilibrium structure with an average intermolecular Li$^+$–D$_2$ separation of 2.035 Å, increasing by 0.003 Å when the D$_2$ subunit is vibrationally excited. The Li$^+$–D$_2$ complex possesses a rotationally resolved D–D stretch band redshifted by 79 cm$^{-1}$ from the fundamental of the D$_2$ diatomic molecule.

From rovibrational line broadening a lower limit for the predissociation lifetime for Li$^+$–D$_2$ is 150 ps. The authors are most grateful to Professor Gianturco and Professor Tantardini for supplying the MTBG Li$^+$–H$_2$ PES.

IV. CONCLUSIONS

The main conclusions of this work can be summarized as follows:

1. The Li$^+$–D$_2$ complex possesses a rotationally resolved D–D stretch band redshifted by 79 cm$^{-1}$ from the fundamental of the D$_2$ diatomic molecule.

2. The Li$^+$–D$_2$ complex has a T-shaped equilibrium structure with an average intermolecular Li$^+$–D$_2$ separation of 2.035 Å, increasing by 0.003 Å when the D$_2$ subunit is vibrationally excited.

3. From rovibrational line broadening a lower limit for the predissociation lifetime for Li$^+$–D$_2$ is 150 ps.

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See EPAPS Document No. E-JCPSA6-125-012627 for a table listing the measured transition wavenumbers for the D–D stretch band of Li$^+$–D$_2$. Given in brackets are the differences between the experimental values and values calculated using an A-reduced Watson Hamiltonian and the parameters in Table I of the paper. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).