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# An infrared spectrum of the molecular dication (doubly positively charged molecule), $\text{D}^{35}\text{Cl}^{2+}$

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We have observed an infrared spectrum within the  $X^3\Sigma^-$  state of  $\text{DCl}^{2+}$  using a fast-ion-beam/laser-beam spectrometer. A preliminary analysis shows good agreement with the rotational constants and tunneling lifetimes calculated by Bennett and McNab for the  $\nu=1-2$  vibrational band, although the calculated band origin appear to be in error by  $21.1\text{ cm}^{-1}$ . © 1998 American Institute of Physics. [S0021-9606(98)03905-1]

Molecular dications may be important in the ionosphere<sup>1</sup> and may be candidates for excimer lasers<sup>2</sup> or even rocket propellants.<sup>3</sup> Molecular dications have been the subject of recent increasing experimental and theoretical effort and interest.<sup>4</sup> Before this work rotationally resolved spectra of only two molecular dications were known,  $\text{N}_2^{2+}$ <sup>5</sup> and  $\text{NO}^{2+}$ <sup>6</sup>; a high resolution spectrum of  $\text{CO}^{2+}$  may have been discovered.<sup>7</sup> As a test of theory, we examine the infrared spectrum of the ground state of  $\text{DCl}^{2+}$ , where our calculations<sup>8</sup> show that *only* tunneling lifetimes should be important in determining the linewidth.

The potential energy (p.e.) curves for doubly charged diatomic molecules are unusual; Fig. 1 shows an *ab-initio* p.e. curve for the  $X^3\Sigma^-$  state of  $\text{DCl}^{2+}(\text{HCl}^{2+})$ .<sup>8</sup> The dissociation asymptote corresponds to the Coulomb explosion of  $\text{Cl}^+$  and  $\text{D}^+(\text{H}^+)$ . All of the vibration-rotation levels lie above the dissociation limit and are therefore quasibound. In previous work<sup>8</sup> we found that the deuterium isotopomers,  $\text{DCl}^{2+}$  should have an extensive spectrum observable with our spectrometer, but that tunneling lifetimes for the hydrogen isotopomers were significantly different, and made observation of their spectrum less likely. We calculate the tunneling lifetimes for the uppermost ( $\nu=4, J=7$ ) and ground ( $\nu=0, J=0$ ) vibration-rotation levels of the ground state of  $\text{D}^{35}\text{Cl}^{2+}$  to be  $1.1 \times 10^{-13}\text{ s}$  and 6.5 h. A theoretical spectrum of  $\text{D}^{35}\text{Cl}^{2+}$  therefore displays the widely differing linewidths that are characteristic of predissociation. When the observed spectrum has been fully assigned, the linewidths should prove valuable in constructing an experimentally modified p.e. function.

Vibrational spectra of  $\text{HCl}^{2+}$  have been obtained in both Auger<sup>9</sup> and threshold photoelectrons in coincidence

(TPESCO) studies.<sup>10</sup> Both studies observed 5 vibrational levels, but our p.e. curve is found to support only 3 vibrational levels (for  $\text{HCl}^{2+}$ ) and we believe that this is a theoretical *upper limit* because the depth of the potential well below the barrier maximum decreases with increasing basis set size.

We have constructed a fast-ion-beam/laser-beam spectrometer; for a general discussion of the advantages of fast ion beam spectroscopy see, for example, McNab.<sup>11</sup> A schematic plan section of the spectrometer is given in Fig. 2. We form  $\text{DCl}^{2+}$  by electron impact ionization of  $\text{DCl}$  in a Vacuum Generators “In-Line” ion source, the two isotopes of chlorine lead to a 3:1 mixture of the isotopomers  $\text{D}^{35}\text{Cl}^{2+}:\text{D}^{37}\text{Cl}^{2+}$ . The pressure in the source chamber is typically  $10^{-5}$  Torr and we estimate the pressure within the source to be  $10^{-4}$  Torr. The ions are accelerated by 0.5–10 kV and are then mass/charge analyzed with a  $53^\circ$  magnetic sector. The magnetic is set to transmit ions with the desired mass/charge ratio which are focused into a 20 cm “drift” tube; this region is maintained at a pressure of less than  $10^{-8}$  Torr.

In the drift tube the ions interact with a collinear, fixed

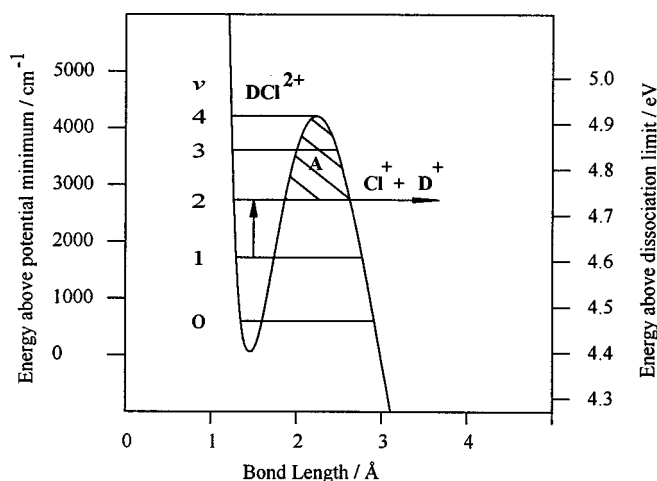


FIG. 1. The p.e. curve for the  $X^3\Sigma^-$  ground electronic state of  $\text{DCl}^{2+}$ . In our experiment a resonant photon transfers population from a long-lived state to one of a shorter lifetime, resulting in an increase in the number of fragments. The fragments undergo Coulomb explosion with a characteristic kinetic energy release.

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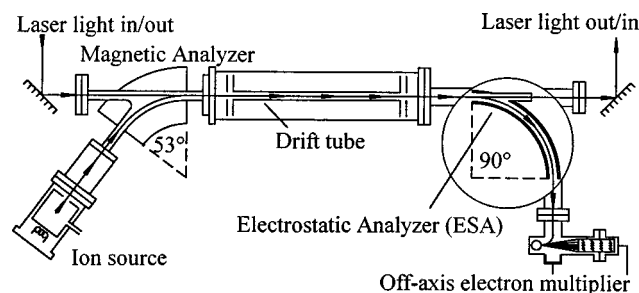


FIG. 2. A schematic diagram of the spectrometer. Ions are formed by electron impact and the mass/charge selected and interacted with a laser beam. Fragment ions are selected by their kinetic energy/charge ratio and detected with an off-axis electron multiplier.

frequency, carbon dioxide laser beam which is obtained from a line tunable Edinburgh Instruments PL3 laser. The laser beam is focused with a zinc selenide lens and admitted into the beam-line through zinc selenide windows. We achieve effective frequency scanning through the Doppler effect—a scan voltage (0 to  $\pm 500$  V) is applied to the drift tube which therefore retards or accelerates the ion beam. The laser beam is chopped to enable lock-in detection.

On resonance an increased rate of  $\text{Cl}^+$  and  $\text{D}^+$  fragmentation is obtained as population transfer from a long-lived state to a shorter-lived state occurs. Transitions are observed as an increase in the fragmentation rate at a particular effective laser frequency. We usually choose to monitor the  $\text{Cl}^+$  fragments which are selected using a  $90^\circ$  cylindrical plate electrostatic analyzer (ESA), and detected using an off-axis electron multiplier. The ESA has a small hole bored in its outside plate in order to allow the laser beam to pass through it; this does not appear to have affected the resolution of the ESA significantly. The ESA is a kinetic energy/charge analyzer, and with the spectrometer “on-resonance” with a particular transition we can record the kinetic energy spectrum of the  $\text{Cl}^+$  or  $\text{D}^+$  photofragments in the laboratory frame (as the resolution of such analyzers is far higher at low kinetic energies we now monitor the light,  $\text{D}^+$ , fragment), a simple transformation then enables the center-of-mass kinetic energy release of the fragments to be determined. Our frequency coverage is governed by the laser lines and Doppler tuning range available; using both  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  we have approximately 50% coverage of the wave number range from 880 to 1090  $\text{cm}^{-1}$  for the isotopomers of  $\text{HCl}^{2+}$ . The disadvantages of this partial coverage can be overcome, to some extent, by examining systems with many fine structure splittings: the chance of finding at least one of the fine structure components is greatly increased given a favorable ratio of the fine structure splittings to laser line separations.

Given the historical difficulty that measurements of dissociation spectra have presented, it is worth making some comments about the sensitivity and resolution of our experiment. Typical beam currents of  $\text{DCl}^{2+}$  are of the order of  $10^{-10}$  amps, corresponding to  $10^8$  molecules per measurement interval of 0.25 s. The squares of the transition dipole matrix elements for our transitions are calculated *ab initio* to be  $\sim 0.5$  D<sup>2</sup> and we can detect the most intense lines with signal to noise ratios greater than 10:1 using laser powers of

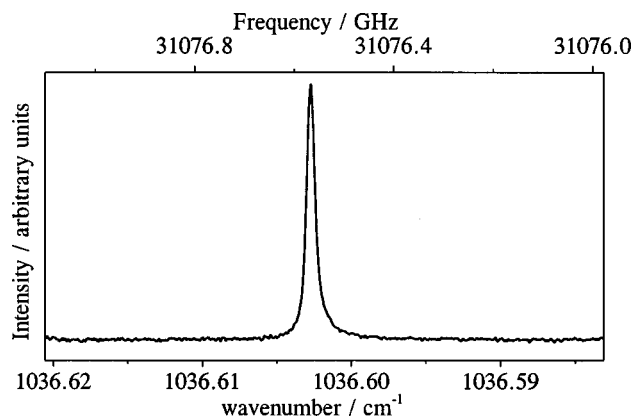


FIG. 3. One of the most intense transitions so far observed, with  $I_{\text{rel}} = 358\,280$ .

10 mW. We have no absolute measurement of even relative line intensities, but for practical purposes we *assume* that the noise level across the spectrum is constant and define the “integrated” relative intensity,

$$I_{\text{rel}} = (S/N) \times \text{width} / \text{laser power},$$

when the laser power is low enough to ensure that this figure is independent of laser power. The transitions are easily saturated and we therefore record transitions at the lowest possible laser powers. The measurement of  $I_{\text{rel}}$  in this manner is fraught with difficulty and between different scans  $I_{\text{rel}}$  is only reproducible to within a factor of 5 or so. Nevertheless, the strongest transition that we have observed has  $I_{\text{rel}} = 549\,780$  whereas weakest transition has  $I_{\text{rel}} = 39$  and this measurement is therefore a useful guide to the intrinsic transition strength.

Line positions are reproducible to within 20 V, corresponding to an instrumental wave number uncertainty of 45 MHz at 5000 V beam potential; this poor reproducibility occurs between scans taken at widely separated times and is due to slightly different settings of the extraction field within the ion source. However, where we can record lines on a single scan the separations can be determined to within 5 MHz. The resolution of the experiment is limited by the velocity distribution of ions in the beam and our maximum resolution is about 10 MHz. Unfortunately it is not possible to degrade the resolution of the experiment, and consequently to scan the full wave number range available to us requires a person-year of effort.

We have recorded 35% of the wave number region between 922 and 1087  $\text{cm}^{-1}$ , and we have located 121 lines in the spectrum of  $\text{D}^{35}\text{Cl}^{2+}$ . We believe that the lines belong to at least 10 vibration–rotation transitions (each vibration–rotation transition is split into six fine structure components due to the spin–spin and spin–rotation interactions present in a  $^3\Sigma$  state; there are also further splittings that we attribute to hyperfine interactions with the chlorine nucleus).<sup>12</sup> Figure 3 shows one of the strongest transitions that we have recorded, taken at a laser power of 10 mW. The line at 1036.603  $\text{cm}^{-1}$  has a relative intensity of 358 280 and a width (FWHM) of 21.2 MHz.

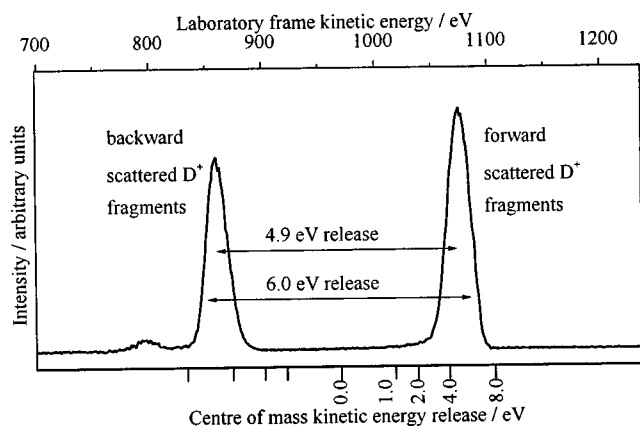


FIG. 4. A kinetic energy spectrum of  $D^+$  fragments obtained while a transition of  $D^{35}Cl^{2+}$  was resonant illustrating the forward-backward scattering along the detection axis, the smallest peak is due to nonresonant  $D^+$  fragments formed within a region with a different electrical potential to the drift tube.

The fine structure that we observe is consistent with a  $^3\Sigma^- - ^3\Sigma$  spectrum. Further confirmation of the assignment is obtained by comparing the measured kinetic energy release with that expected from fragmentation of the  $X^3\Sigma^-$  state. The expected energy release is estimated by combining measurements of the first ionization potentials of D and Cl (13.59 and 12.96 eV),<sup>13</sup> together with the dissociation energy,  $D_0$ , of DCl (4.48 eV)<sup>15</sup> and the double ionization energies  $T_{00}$  (35.59 eV) for the formation of  $HCl^{2+}$  (DCl<sup>2+</sup> information being unavailable) from neutral HCl<sup>10</sup> and the calculated well depth ( $D_e = 0.54$  eV) for the  $^3\Sigma$  state; the expected kinetic energy release will be between 4.55 eV [ $= T_{00} - I_1(D) - I_1(Cl) - D_0(DCl)$ ] and 5.09 eV [ $= T_{00} + D_e - I_1(D) - I_1(Cl) - D_0(DCl)$ ]. These estimates may be compared with the theoretical energies above dissociation shown on the right hand axis of Fig. 1. Figure 4 shows a typical kinetic energy spectrum obtained on-resonance; the two peak structure is due to forward and backward scattered fragments relative to the direction of the beam passing into the entrance of the ESA. Our measured center-of-mass kinetic energy release is between 4.96 and 5.99 eV, depending where on the peaks is taken to be the correct measurement point. The measured and expected kinetic energy releases are consistent.

Unfortunately our kinetic energy resolution is not sufficient to allow us to determine the vibrational levels involved in fragmentation, and we have assigned the band system using a comparison of theoretical and experimental vibrational band structure. Figure 5 shows a stick spectrum of the most intense experimentally observed transitions (which should correspond to the  $P$  and  $R$  triplets of the fine structure pattern), together with an *ab-initio* theoretical spectrum of the  $\nu=2-1$  band (neglecting triplet splittings). The values of the rotational constants in the theoretical spectrum are (in  $cm^{-1}$ )  $B_1 = 3.898$ ,  $D_1 = 3.561 \times 10^{-4}$ ,  $H_1 = 1.04 \times 10^{-9}$ ;  $B_2 = 3.648$ ,  $D_2 = 3.163 \times 10^{-4}$ ,  $H_2 = -9.269 \times 10^{-8}$ . To match the observed and calculated spectra it was necessary to shift the band origin of the theoretical spectrum ( $1015.4\text{ cm}^{-1}$ ) by  $-21.1\text{ cm}^{-1}$ . The agreement between

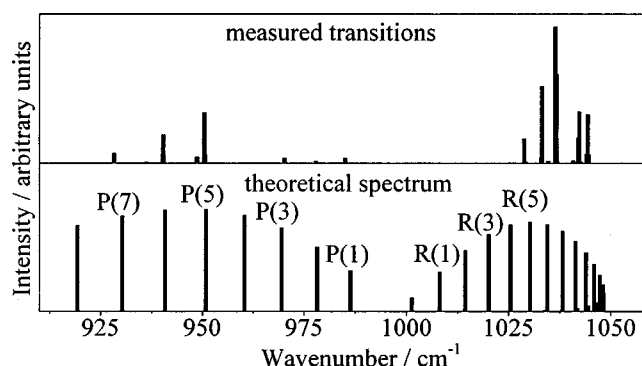


FIG. 5. A stick spectrum of observed transitions and intensities, together with a theoretical spectrum (neglecting fine and hyperfine structure), which is shifted by  $-21.1\text{ cm}^{-1}$  from the theoretical band origin.

the calculated and measured spectra is fair (considering that no theoretical allowance for the triplet fine structure was made) and we are persuaded that we are observing the  $\nu=2-1$  band of  $D^{35}Cl^{2+}$ . Observation of the  $D^{37}Cl^{2+}$  spectrum is in progress<sup>14</sup> and we hope this will enable an experimental determination of the vibrational band system from the vibrational isotope shift.<sup>15</sup>

The band origin of the observed spectrum appears to lie in a wave number range ( $990-1021\text{ cm}^{-1}$ ) that is not currently accessible to us (lying between the  $00^{\circ}1-10^{\circ}0$   $R$  branch and the  $00^{\circ}1-02^{\circ}0$   $P$  branch of  $^{12}CO_2$ ), and we cannot yet be certain of the rotational numbering of the observed transitions because any consistent set of rotational quantum numbers allows a determination of rotational constants.<sup>15</sup> We are in the process of altering our apparatus to include a solenoid to induce Zeeman splitting of the lines, from which we hope to determine the total angular momentum of the states involved.

The physical dimensions of our ion-beam spectrometer impose a limit on both the upper-state and lower-state lifetimes that we can observe (see, for example, Ref. 11). The initial state must be sufficiently long-lived for a reasonable population to survive the time of extraction from the ion source, and transport to the drift tube ( $\tau_i \geq 10^{-6}\text{ s}$ ) and the final state must be sufficiently short lived for significant fragmentation to occur within the drift tube ( $\tau_f \leq 10^{-7}\text{ s}$ ). The linewidths of our measured transitions vary from 8 to 255 MHz corresponding to a variation in upper state lifetimes of  $2 \times 10^{-8} - 6 \times 10^{-10}\text{ s}$ . The instrumental linewidth is determined primarily by the velocity distribution of ions leaving the ion source, which maps onto a frequency distribution through the Doppler effect; 8 MHz probably represents the minimum linewidth observable with our present ion source. The upper levels in the theoretical 2-1 band run from  $\nu=2, J=0$  to  $\nu=2, J=19$  and these levels have tunneling lifetimes of  $6 \times 10^{-7}\text{ s}$  to  $8 \times 10^{-10}\text{ s}$ ; the ranges of the measured and theoretical linewidths are therefore in good agreement. This agreement is strong evidence for the quality of our p.e. function: The widths are exponentially dependent on a quantity closely related to the area under the barrier at a particular resonance energy (represented by the shaded area "A" on Fig. 1), and hence upon the barrier width.

Our measurements are the first rotationally resolved in-

frared measurements of a molecular dication spectrum. With appropriate frequency sources our technique could easily be extended to the visible, microwave and radio-frequency regions. The full analysis of our spectrum will enable more stringent tests of p.e. functions (from transition energies and linewidths) and calculated wave functions (from hyperfine constants) than has hitherto been possible. Our preliminary analysis shows that our p.e. function is of high quality, and casts further doubt on the assignment of the earlier, vibrationally resolved spectra of  $\text{HCl}^{2+}$ .

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