4 June 1999

Chemical Physics Letters 306 (1999) 48–52

CHEMICAL PHYSICS LETTERS

Cl_3^- electron photodetachment spectrum: measurement and assignment

Alexey L. Kaledin [a], Michael C. Heaven [a], Keiji Morokuma [a,*], Daniel M. Neumark [b]

[a] Cherry L. Emerson Center for Scientific Computing and Department of Chemistry, Emory University, Atlanta, GA 30322, USA
[b] Department of Chemistry, University of California, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Received 25 January 1999; in final form 15 March 1999

Abstract

An electron photodetachment spectrum of Cl_3^- is reported for 193 nm (6.42 eV) excitation. The spectrum was assigned using high-level ab initio calculation for the Cl_3 radical and the Cl_3^- ion. A broad band centered around 1.25 eV (electron kinetic energy) has been assigned to the $Cl_3^-(X\,^1\Sigma_g^+) \rightarrow Cl_3(X\,^2\Pi_u)$ and $Cl_3(1\,^2\Sigma_g^+)$ transitions. Vertical photodetachment accesses the transition state region for the Cl exchange reaction: $Cl + Cl_2 \rightarrow Cl_2 + Cl$. A narrow doublet band at 0.55 eV is assigned to the $Cl_3^-(X\,^1\Sigma_g^+) \rightarrow Cl_3(1\,^2\Pi_g)$ transition, split by spin–orbit interaction. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Indirect evidence for the existence of bound Cl_3 was originally derived from studies of Cl atom recombination kinetics [1]. However, recent theoretical studies have shown that the ground state Cl_3 is very weakly bound [2–5]. It is best thought of as a $Cl_2 \cdots Cl$ van der Waals complex. The low-lying excited states of Cl_3 are also unstable, with the exception of one state that has a linear symmetric equilibrium geometry ($1\,^2\Pi_g$) [4]. There is no clear evidence that neutral Cl_3 has ever been observed [4,6]. The weakness of binding in the ground state, less than 1 kcal/mol, makes it a challenging case for IR techniques [4,7]. The absence of stable excited states that are Franck–Condon accessible makes Cl_3 challenging for UV studies [4].

Anion photodetachment spectroscopy provides a more promising means for observing the ground and low-lying states of Cl_3. The Cl_3^- anion is stable in the ground state [3] and can be studied experimentally in the gas phase [8–10]. The ground state has a linear symmetric structure with a bond length of ~ 2.3 Å [3,11,12]. Vertical photodetachment from this geometry is expected to access the ground state at a geometry appreciably displaced from the van der Waals minimum, and the $1\,^2\Pi_g$ state near the bottom of its potential energy well. In this Letter we report a photodetachment spectrum for Cl_3^- taken using 193 nm excitation. Results from high-level ab initio calculations have been used to assign this spectrum.

---

[*] Corresponding author. Fax: +1 404 727 6586; e-mail: morokuma@emory.edu

PII: S0009-2614(99)00419-4

2. Technical details

2.1. Experimental

The negative ion photoelectron spectrometer used in these experiments has been described in detail previously [13]. A mixture of 5% Cl_2 in Ar was expanded through a pulsed nozzle. Negative ions were generated by a 1 keV electron beam, which crossed the expansion close to the nozzle. Cl_3^- anions were mass-selected by time-of-flight, and photodetached by an excimer laser operating at a wavelength of 193 nm (6.42 eV). Photoelectrons were detected at the end of a 1 m long field-free flight tube. Electron kinetic energies were determined from the flight times. Extensive signal averaging was used to obtain the spectrum, which was recorded using 240000 laser pulses.

2.2. Considerations in electronic structure calculations

In our previous theoretical study of the trichlorine radical [4], we learned that a high-level electron correlation method is essential for predictions of low-lying electronic states with near quantitative accuracy. Such properties as term energies and internuclear distances could only be obtained with good accuracy by a multireference configuration interaction method combined with an extensive basis set. Furthermore, diffuse orbitals are required to adequately describe the anion. In the present study of the $Cl_3 + \bar{e} \leftarrow Cl_3^-$ excitation spectrum, we used the multireference internally contracted singles and doubles configuration interaction [14,15] with Davidson correction for size-consistency [16,17]. MRSDCI(D), to calculate the potential energy curves of both the anion and the neutral. We used the Dunning correlation-consistent valence triple-zeta polarized basis set augmented with diffuse orbitals, cc-avtz [18]. The molecular orbitals (MO), were generated using the complete active space self-consistent field (CASSCF) [19–21] method. This included 21 electrons (22 for the anion) distributed among 12 molecular orbitals consisting of 3s3p orbitals on each chlorine atom. State-averaging was used in the CASSCF procedure to generate orbitals of the radical. Consequently, the three spatial components of $X\,^2\Pi_u$ and $1\,^2\Sigma_g^+$ states of Cl_3 were state-averaged with equal weights to generate reference wavefunctions for the MRSDCI procedure. In a separate calculation, the $1\,^2\Pi_g$ degenerate components were state-averaged for the subsequent MRSDCI calculation. The reference function for MRSDCI was the converged CASSCF wavefunction, whose size varied from 70 to 90 configuration state functions (CSF) for the radical and 20 CSFs for the anion. Electronic configurations and potential energy surfaces for Cl_3 were presented in Ref. [4].

Spin–orbit interaction for the radical was calculated using a perturbation theory approach, as described in Ref. [22]. We considered interactions between the $X\,^2\Pi_u$, $^2\Sigma_g^+$, and $^2\Pi_g$ states, resulting in a 10×10 spin–orbit CI matrix. For evaluation of spin–orbit matrix elements we used CASSCF wavefunctions with a smaller basis set, TZ2P [23]. Nonrelativistic calculations (spin-free Hamiltonian) were performed with the MOLPRO [24] package version 96.4, while spin–orbit calculations were performed using version 98.1.

3. Results and discussion

3.1. Photodetachment spectrum

The spectrum appearing in Fig. 1 represents the kinetic energy distribution of the detached electrons

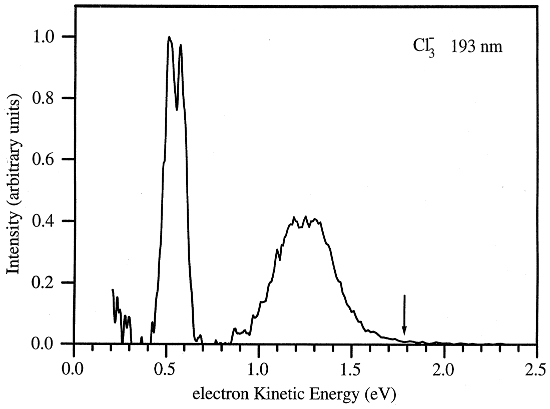

Fig. 1. The 193 nm photodetachment spectrum of Cl_3^-. The horizontal axis is the kinetic energy of the detached electron in eV. The vertical axis is proportional to the flux of electrons. The arrow indicates the threshold for ionization. The structure to the left of the sharper peak is probably due to noise.

after photolyzing Cl_3^- at 193 nm (6.42 eV). The resolution of this spectrum (≈ 0.01 eV) was determined by the bandwidth of the excitation source. The relationship between the kinetic energy of the detached electron (E_{kin}) and the corresponding energy of the vibronic level of Cl_3 relative to ground state of Cl_3^- (E_{Cl_3}) can be written as,

$$h\nu - E_{\mathrm{kin}} = \mathrm{IP} + E_{Cl_3},$$

where $h\nu$ is the photon energy, and IP is the lowest adiabatic ionization potential of Cl_3^-. In the following, energies derived from Fig. 1 are given as E_{kin}, with $\mathrm{IP} + E_{Cl_3}$ in brackets.

Note that the entire photodetachment spectrum represents excitation to Cl_3 levels that have enough energy to dissociate to $Cl_2 + Cl$. Nizzi et al. [8]. reported a dissociation energy of 1.03 ± 0.05 eV for $Cl_3^- \rightarrow Cl_2^- + Cl$. Given the photon energy of the laser (6.42 eV) and the electron affinity [25] of Cl (3.61 eV), features in the photodetachment spectrum at electron kinetic energies < 1.78 eV corresponds to states of the neutral with enough energy to dissociate.

There are two well-defined features in Fig. 1: a broad band centered at 1.25 [5.17] eV and a sharper doublet at 0.55 [5.87] eV. The width (0.35 eV FWHM) and shape of the broad feature suggests excitation to repulsive region of the Cl_3 state (or states) involved. The sharper structure of the doublet suggests excitation to bound levels. The doublet splitting (0.066 eV) could be interpreted in terms of transitions to two separate electronic states, vibrational structure, or spin–orbit splitting.

3.2. Comparison with ab initio calculations

The method used to generate Cl_3^- should produce vibrationally cold anions, so we assume that the main features in the spectrum arise from the zero-point vibrational level of $Cl_3^-(X\,^1\Sigma_g^+)$. We also assume that the spectrum represents a vertical ionization process (i.e., the nuclei do not move during photodetachment). To make comparisons with the ab initio calculations, we consider cuts through the potential energy surfaces along the symmetric stretch coordinate. Fig. 2 shows cuts for $Cl_3^-(X\,^1\Sigma_g^+)$ and selected low-lying states of $Cl_3(X\,^2\Pi_u,\ 1\,^2\Sigma_g^+$, and $1\,^2\Pi_g)$. The energy zero is defined at the minimum of $Cl_3^-(X\,^1\Sigma_g^+)$. Our calculations show that the $D_{\infty h}$ structure is the true minimum for Cl_3^-, with a bond length of 4.41 bohr and dissociation energy (relative to $2Cl(^2P) + Cl^-(^1S)$) of 3.04 eV. The dissociation energy relative to $Cl_2(X) + Cl^-$ can be determined from the $2Cl + Cl^-$ dissociation energy less the $Cl_2(X)$ bond energy (2.36 eV). This cycle yields an estimate of 0.68 eV, as compared to the experimental value of 1.03 eV [8]. The error is surprisingly large, given that the present calculations accurately predict the electron affinity of Cl (3.61 eV calculated, 3.62 eV measured [25]). No doubt, better results could be obtained using a larger basis set, but the accuracy of the present calculation is sufficient for assignment of the photodetachment spectrum.

Three states of Cl_3 neutral correlate with the $Cl_2(X\,^1\Sigma_g^+) + Cl(^2P)$. The lowest state in $D_{\infty h}$ symmetry, $X\,^2\Pi_u$, is 4.96 eV above zero, at $r(\mathrm{Cl{-}Cl}) = 4.36$ bohr. The surface displays a standard Renner–Teller pattern splitting into $^2A_1$ (unstable lower component) and $^2B_1$ (stable upper component) [2]. In C_{2v} symmetry the lower component, which becomes $X\,^2A_1$ and correlates with the van der Waals global minimum, has a stationary point with the angle of 146° and the bond of 4.16 Å [4]. The structure is unstable with respect to the antisymmetric stretch while the minimum in the remaining coordinates ensures the transition state (at 4.59 eV) for the $Cl + Cl_2 \rightarrow Cl_2 + Cl$ exchange reaction. The global minimum for the surface ($C_{\infty\nu}$, $\widetilde{\mathbf{XL}}\,^2\Pi$), is at 4.35 eV. The upper Renner–Teller component is stable with respect to the bending coordinate. This surface supports a linear transition state for the exchange reaction. Almost degenerate with $X\,^2\Pi_u$, the $1\,^2\Sigma_g^+$ state is bound with respect to bending and the symmetric stretch, but it is not stable with respect to asymmetric displacements [4]. It represents another linear transition state for the exchange reaction.

Of the low-lying excited states, only $1\,^2\Pi_g$ is significantly bound. This state has a linear symmetric equilibrium geometry with a bond length of 4.54 bohr. As can be seen in Fig. 2, the minimum of $1\,^2\Pi_g$ is 5.60 eV above $Cl_3^-(X\,^1\Sigma_g^+)$.

The curves shown in Fig. 2 can be used to assign the 193 nm photodetachment spectrum of Cl_3^-. Vertical transitions to the $Cl_3X\,^2\Pi_u$ and $1\,^2\Sigma_g^+$ states should produce features in the spectrum near 1.4 [5.0] eV. These features should be broad and over-

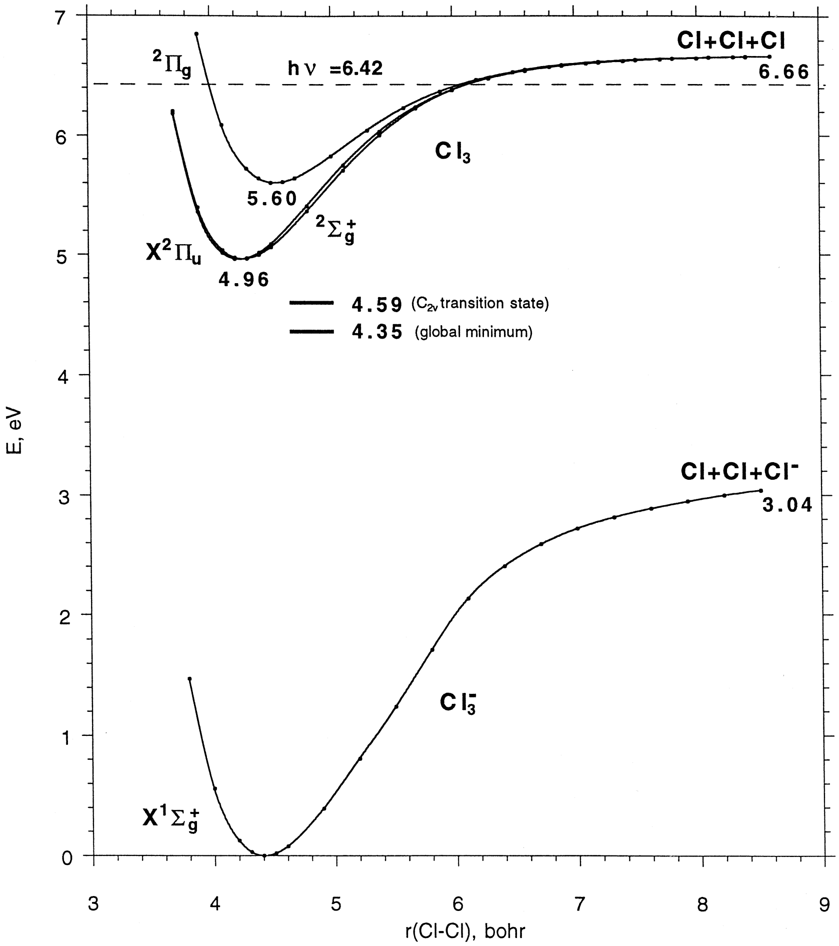

Fig. 2. The Cl_3^- and Cl_3 potential energy curves calculated with MRSDCI(D)/avtz in $D_{\infty h}$ symmetry. The horizontal axis is the distance between two adjacent chlorine atoms in bohr. The vertical axis is the energy in eV, relative to the minimum of $Cl_3^-, X^1\Sigma_g^+$. Numbers in bold represent energies (eV) of specific states of the radical, the asymptotes, and the photon energy (marked with a long-dashed line).

lapped as they terminate on repulsive (unbound) regions of the two states. The high energy cut-off for the broad band is predicted to be at 2.07 [4.35] eV, although a transition to the minimum of Cl_2 $\widetilde{\mathbf{X}}\mathbf{L}$ will have a very small Franck–Condon density. Clearly, these predictions are in reasonable agreement with Fig. 1. Part of the 0.15 eV discrepancy between the predicted and observed center for the broad feature must be associated with the underestimation of the Cl_3^- bond energy.

The doublet at 0.55 [5.87] eV is consistent with a vertical transition to $1\,^2\Pi_g$. Our calculations predict this feature at 0.82 [5.60] eV. Correcting for the underestimated Cl_3^- bond energy gives good agreement between theory and experiment. As there are no bound states overlapping $1\,^2\Pi_g$, we can discount the possibility that the doublet structure is due to transitions to nearby states. The comparable intensities of the peaks suggest spin–orbit splitting, rather than a vibrational progression. As Cl_3^- and Cl_3 have such similar bond lengths, we expect that a transition to a vibrationally excited level would be significantly weaker than the origin band. The observed doublet splitting (0.066 eV) is in reasonable agreement with the spin–orbit interval of 0.074 eV calculated at $r = 4.54$ bohr.

4. Conclusions

The photodetachment spectrum for Cl_3^- has provided the first unambiguous spectroscopic data for the ground and low-lying states of Cl_3. The spectrum is rather simple, in that it shows only two prominent structures. However, both the simplicity of the spectrum and the characteristics of the bands are in good agreement with the predictions of ab initio calculations. Previous theoretical calculations indicated that the lowest energy states of Cl_3 are not bound, and the broad origin band in the photodetachment spectrum is consistent with a transition to a repulsive state. Within the energy range examined, calculations predict only one bound state $(1\,^2\Pi_g)$ that would be accessible. The energy and contour of the second band in the spectrum are entirely consistent with a transition to $1\,^2\Pi_g$.

Acknowledgements

This research was supported by grants from the Air Force Office of Scientific Research (F49620-98-1-0063 (KM), F49620-98-1-0054 (MCH), and F496720-97-1-0018 (DMN)).

References

[1] E. Hutton, M. Wright, J. Chem. Soc. Faraday Trans. 61 (1964) 78.
[2] A.B. Sannigrahi, S.D. Peyerimhoff, Int. J. Quantum Chem. 39 (1986) 423.
[3] T.G. Wright, A.J. Bell, J.G. Frey, Chem. Phys. Lett. 189 (1992) 297.
[4] A.L. Kaledin, M.C. Heaven, W.G. Lawrence, Q. Cui, J.E. Stevens, K. Morokuma, J. Chem. Phys. 108 (1998) 2771.
[5] T.G. Wright, E.P.F. Lee, Mol. Phys. 79 (1993) 995.
[6] W.G. Lawrence, R.M. Fulghum, M.C. Heaven, J. Phys. Chem. 100 (1996) 18702.
[7] Y.T. Lee, R.R. LeBreton, J.D. McDonald, D.R. Herschbach, J. Chem. Phys. 51 (1969) 455.
[8] K.E. Nizzi, C.A. Pommerening, L.S. Sunderlin, J. Phys. Chem. A 102 (1998) 7674.
[9] R. Robbiani, J.L. Franklin, J. Am. Chem. Soc. 101 (1979) 764.
[10] L.C. Lee, G.P. Smith, J.T. Moseley, P.C. Cosby, J.A. Guest, J. Chem. Phys. 70 (1979) 3237.
[11] Y. Ogawa, O. Takahashi, O. Kikuchi, J. Mol. Struct. (THEOCHEM) 424 (1998) 285.
[12] A.B. Sannigrahi, S.D. Peyerimhoff, Chem. Phys. Lett. 141 (1987) 49.
[13] R.B. Metz, A. Weaver, S.E. Bradforth, T.N. Kitsopoulos, D.M. Neumark, J. Phys. Chem. 94 (1990) 1377.
[14] H.-J. Werner, P.J. Knowles, J. Chem. Phys. 89 (1988) .
[15] P.J. Knowles, H.-J. Werner, Chem. Phys. Lett. 145 (1988) 514.
[16] E.R. Davidson, D.W. Silver, Chem. Phys. Lett. 53 (1977) 403.
[17] H.-J. Werner, P.J. Knowles, Theor. Chim. Acta 78 (1990) 175.
[18] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
[19] H.-J. Werner, P.J. Knowles, J. Chem. Phys. 82 (1985) 5053.
[20] P.J. Knowles, H.-J. Werner, Chem. Phys. Lett. 115 (1985) 259.
[21] H.-J. Werner, W. Meyer, J. Chem. Phys. 74 (1981) 5794.
[22] A.L. Kaledin, M.C. Heaven, K. Morokuma, Chem. Phys. Lett. 289 (1998) 110.
[23] A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (1980) 5639.
[24] MOLPRO 96, and 98, H.-J. Werner, P.J. Knowles, University of Birmingham, UK, 1998.
[25] R. Trainham, G.D. Fletcher, D.J. Larson, J. Phys. B: At. Mol. Phys. 20 (1987) L777.