From $1/r$ to $1/r^2$ Potentials: Electron Exchange between Rydberg Atoms and Polar Molecules

C. Desfrançois, H. Abdoul-Carime, N. Khelifa and J. P. Schermann

Laboratoire de Physique des Lasers, Institut Galilée, Université Paris-Nord, 93430 Villetaneuse, France

(Received 4 April 1994)

Several new molecular anions, in their dipole-bound ground states, have been created by charge exchange between polar molecules and laser-excited Rydberg atoms. Measurement of electron-binding energies, by means of electric field detachment, as function of known molecular dipole moments gives the first experimental estimation of the minimum molecular dipole required to bind an electron.

PACS numbers: 34.70.+e, 34.80.−i, 35.20.Vf, 35.80.+s

In an atom, an electron can be bound in an infinite number of discrete states by the $1/r$ Coulomb attraction. Mathematically, an electron can also be bound in a pure $-C/r^2$ potential if $C > \frac{1}{4}$ [1] or in a point-dipole potential $-\mu \cdot \mathbf{r}/r^3$, with $\mu > 1.625$ D but with an infinite number of states with infinite energies [2]. More physically satisfying finite energy bound states appear if the finite size of the dipole is taken into account and if the electron is not allowed to approach too close from the positive end of the dipole. This situation is encountered when an electron is attached to a closed-shell polar molecule, since the Pauli principle then introduces a short-range repulsion of the excess electron, which combines with additional potential terms due to molecular rotation and polarizability. Model potential calculations of Garrett [3] have demonstrated the key role of these effects for very weakly bound anions when the molecular parents have low dipole moments (2–4 D), while *ab initio* calculations [4] have mostly been devoted to strongly polar molecules (4–10 D), some of them having biological significance [5]. The overall result is that it is usually accepted [6] that a neutral molecule with a dipole moment of ~2 D should be able to sustain stable anion. Direct experimental proof of the existence of such dipole-bound systems has come from the observation of resonances in photodetachment studies of several radical anions [7,8]. In these experiments, anions in their valence ground states are photoexcited towards electronically excited dipole-bound states which can rapidly autodetach when their rotational levels lie in the photodetachment continuum. The mechanism for autodetachment has been described by Clary [9], and it has been experimentally demonstrated that the binding of an electron is very sensitive to the molecular geometry and the motion of the dipole [10].

Direct dipole-bound anion formation by electron attachment to a closed-shell polar molecule with negative electron affinity in its ground state is an alternative which does not necessitate an exacting spectroscopic requirement. Thus this technique enlarges the range of molecules which can be explored. Another advantage is that the relevant molecular constants (dipole moment, polarizability, and rotational constants) are well established for the neutrals and do not rely on calculations. However, the observation of ground-state dipole-bound anions has long proven an experimental difficulty [11], due to the very diffuse character of the orbital carrying the excess electron. The nuclear configurations of the neutral parent molecule and the weakly bound anion are virtually identical, and the presence of a third-body stabilizing against autodetachment is necessary. For a long time, the only observed ground-state dipole-bound systems were the acetonitrile anion [11–13] and the water dimer anion [14], but the only measured electron binding energy was that of $(H_2O)_2^-$ [15]. We have recently been able to measure the electron-binding energies of two ground-state dipole-bound systems, i.e., the water-ammonia dimer [16] and the acetonitrile anions [17], by creating them in charge-transfer collisions with laser-excited Rydberg atoms. These atoms constitute a source of well-controlled low energy electrons, and their ionic core acts as the third body. We report here the results of the first extensive set of measurements of low electron-binding energies of ground-state dipole-bound anions in order to set an experimental lower value of the critical molecular dipole required to bind an electron.

The crossed-beam experiment used in this study has been described previously [18]. A pulsed beam of metastable xenon atoms is excited towards Rydberg nf states by means of a tunable dye laser. The Rydberg atoms collide with a pulsed beam of polar molecules seeded in helium. Ions created by charge exchange are extracted from the collision region and are further accelerated and focused into a detector situated at the end of a time-of-flight mass spectrometer. Accelerating and focusing fields can be lowered to 15 V/cm to allow for the observation of very weakly bound anions. The n dependences of the rate constants for the creation of molecular anions created in reactions $\mathrm{Xe}(nf) + M \rightarrow \mathrm{Xe}^+ + M^-$ are obtained by comparison with SF_6^- signals in collisions with SF_6 [18,19]. The center-of-mass collision energy is 350 ± 20 meV, and the rotational temperature of the molecules is estimated to lie between 5 and 10 K. The time delay between the opening of the molecular beam and the Rydberg atom creation is tuned in order to prevent any cluster formation [17].

0031-9007/94/73(18)/2436(4)$06.00

We have chosen the study of aldehydes, ketones, and cyanides since they are closed-shell molecules with available dipole moments [20], which lie between 2 and 4 D. Some of them, such as acrolein, were directly discarded since their electron affinities were already known to be positive [4]. For the others, the presence of a dipole-bound state was experimentally detected by the shape of the n dependency of the anion formation rate constant. Pyruvonitrile, for instance, gives birth to previously unobserved anions with a smooth creation rate n dependency over the whole $n = 7$ to 70 explored range and thus behaves like molecules which are known to possess positive electron affinities [18,19,21]. On the contrary, the anions reported here exhibit n dependences of their creation rates, which are strongly peaked (Fig. 1) as for the previously reported acetonitrile anion [17]. The peak n values do not directly correspond to the thermoneutral values (equality of the Rydberg atom ionization potential and the anion electron-binding energies), but they are approximately correlated to the molecule dipole moments μ (small μ values correspond to large peak n values). In order to ascertain the dipole-bound nature of these anions, field detachment measurements have been performed. When anions possess very small binding energies (≤ 1 meV), acceleration and focusing fields are increased until they are large enough to detach anions totally. The nondetection thus directly provides a measure of the critical electric detachment field. For larger values of the electron-binding energies, electric field detachment is performed by means of a set of three grids perpendicular to the ion path [16]. In both cases we calculate the quasiclassical tunneling probability of the excel electron in a bound negative-ion state, with binding energy E_b, through the potential-energy barrier lowered by the external electric field when the molecular dipole moment and the applied field are antiparallel. We thus obtain experimental E_b values by fitting the experimental field detachment probability curves. In all cases, we observe only one sharp transition in these curves, suggesting that anions are always created in a single ground state. This confirms a prediction of Garrett [22] which states that the infinite number of excited electronic states existing in the fixed nuclear approximation shrinks to only one for low dipole values (≤ 3 D) when nuclear motion is included. Critical detaching fields are determined with a precision better than 10%, but, as previously discussed [17], the above E_b determination can be altered by dynamical processes occurring during the field detachment process. Since anion and neutral configurations are expected to be almost identical, these E_b values can be considered as estimates of the adiabatic electron affinities.

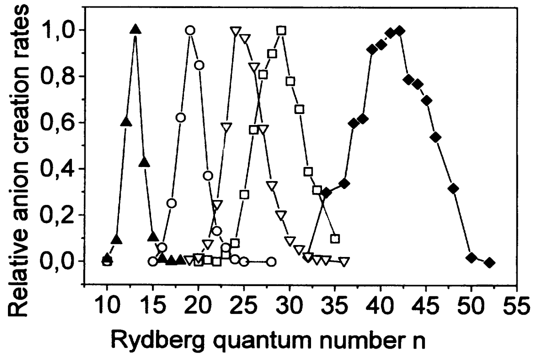

FIG. 1. The n dependences of relative rate constants for the formation of acetonitrile (filled triangles), cyclohexanone (open circles), acetone (open triangles), cyclobutanone (open squares), and acetaldhyde (diamonds) anions in collisions of Xe** (nf) atoms.

The obtained E_b values (Table I) almost cover our experimental range which is determined by the minimum electric field in the time-of-flight spectrometer (15 V/cm) and the maximum detachment field we can apply (30 kV/cm). For a μ/r^2 binding potential, the critical detachment field F is classically related to the electron-binding energy E_b by the expression (in a.u.) $27\mu F^2/4 = E_b^3$. Our measured E_b values lie between 0.1 and 17 meV. Even if larger dipole moments correspond to larger E_b values (e.g., cyanide compounds), rather different E_b values can be associated with the same dipole moment μ (see, ketones and trifluoromethylbenzene). This means that general trends can be deduced from a large set of measurements while individual E_b values also depend on specific properties other than μ for each individual molecule. The lowest molecular dipole giving an experimentally observed anion is here $\mu = 2.66 \pm 0.06$ D (pivaldehyde), while we did not observe propanal or formaldehyde anions (2.52 and 2.33 D).

Ab initio calculations of such small electron affinities are still very difficult but, as shown by Garrett [3], rather accurate E_b values can be derived from a pseudopotential method. More recently, Clary described a simple method leading to accurate energy levels and autodetachment widths for dipole-bound anions of symmetric top molecules [9]. Along these guidelines, we performed model calculations as follows. We take the excess electron-molecule pseudopotential as $V(r,\theta) = V_\mu(r,\theta) + V_\alpha(r) + V_{\rm SR}(r)$, where r and θ are the excess electron cylindrical coordinates with respect to the molecular symmetry axis, and V_μ, V_α, and $V_{\rm SR}$ are the dipolar, charge-induced dipole, and short range potential terms which are expressed as (in a.u.)

$$\begin{aligned} V_\mu(r,\theta) &= -\mu\cos\theta/r^2 \quad \text{for } r > \mu/2, \\ V(r,\theta) &= -8r\cos\theta/\mu^2 \quad \text{for } r < \mu/2, \\ V_\alpha(r) &= -(\alpha/2r^4)f(r), \end{aligned}$$

where

$$f(r) = 1 - \exp[-(r/r_0)^6],$$

$$V_{\rm SR}(r) = V_C\exp[-(r/r_c)^6].$$

TABLE I. Experimental electron binding energies of molecular anions measured by field detachment. Formaldehyde and propanal anions were not observed (see text).

Molecule	μ (D)	E_b (meV)
Formaldehyde HCHO	2.33	< 0.1 (not obs.)
Propanal CH_3CH_2CHO	2.52	< 0.1 (not obs.)
Pivaldehyde$(CH_3)_3CCHO$	2.66	0.50
Butanal $CH_3(CH_2)_2CHO$	2.72	0.7
Acetaldehyde CH_3CHO	2.75	0.36
2-butanone $CH_3CH_2COCH_3$	2.78	1.0
Trifluoromethylbenzene $C_7H_5F_3$	2.86	2.2
Cyclohexanone $C_6H_{10}O$	2.87	3.3
Acetone CH_3COCH_3	2.88	1.5
Cyclopentanone C_5H_8O	2.88	1.7
Cyclobutanone C_4H_6O	2.89	1.0
Methylacrylonitrile CH_2CCH_3CN	3.69	6.3
Acrylonitrile CH_2CHCN	3.87	6.9
Acetonitrile CH_3CN	3.92	11.5

As can be seen from these expressions, V_μ and V_α vanish for r values lower than $\mu/2$ and r_0, respectively, while V_{SR} tends to $V_c > 0$ for $r < r_c$, thus taking into account the short-range repulsion due the Pauli exclusion principle. In order to restrict the number of pseudopotential parameters and because they are not all independent from each others, we take $r_0 = \alpha^{1/3}$ and $V_c = 1$ a.u., keeping only μ, α, and r_c as actual physical parameters. Electron-binding energies are then calculated using Clary's rotationally adiabatic theory [9] with total angular momentum $J = 0$, since E_b does not depend on J but only on the molecular rotational constant B and the above pseudopotential parameters. The calculated E_b values are displayed in Fig. 2 as a function of the dipole moment μ for two sets of molecular parameters, together with all known experimental values from our measurements (Table I), those of Lineberger *et al.* for cyanomethyl [7], acetaldehyde enolate [8], and alkali halide anions [23] and Bowen *et al.* measurement for LiH^- [24]. The first set of parameters ($r_c = 2.7$ a.u., $B = 1\ cm^{-1}$, $\alpha = 4\ Å^3$) is suitable for small diatomic anions (such as LiH^- and $LiCl^-$), while the second set ($r_c = 4.2$ a.u., $B = 0.1\ cm^{-1}$, $\alpha = 8\ Å^3$) corresponds to molecular parameters for heavier diatomics (e.g., $CsCl^-$) and for most molecules of the present work. Except for very large polar molecules for which the parameter r_c should be larger than 4.2 a.u., the two displayed curves should correspond to the region inside which observation of molecular dipole-bound anions can be expected. If we set a lower physical limit to E_b equal to the rotational constant B, we thus conclude that the minimum dipole moment required to bind an extra electron must lie between 2.0 and 2.2 D.

This result is in very good agreement with the original predictions of Garrett [3] and Crawford [6] who suggested that "any real gas phase molecule or radical with $\mu \geq 2$ D probably can bind an electron and almost certainly if $\mu > 2.5$ D." We might, nevertheless, stress the experimental difficulties which one would encounter in exploring the region between 2.0 and 2.5 D. Light diatomics with dipole moment in this range do not seem to exist, and one must then deal with heavy diatomics or polyatomic molecules for which the corresponding electron-binding energies should lie between 0.01 and 0.1 meV and with rotational constants B around 0.1 cm^{-1}. Such weak binding energies would require external electric fields used for mass selection lower than 0.5 and 15 V/cm,

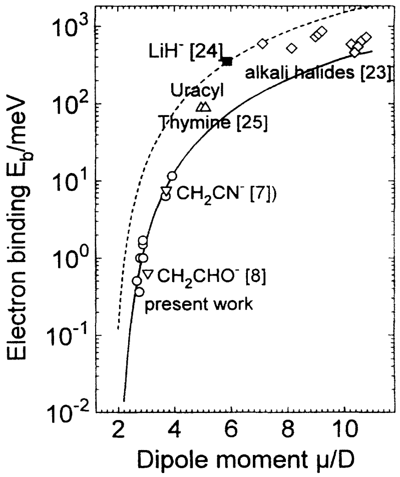

FIG. 2. Electron-binding energies of molecular anions as a function of parent molecular dipole moments. Solid and dashed lines correspond to results of pseudopotential calculations, respectively, for "large" and "small" molecules (see text). Down triangles correspond to excited dipole-bound anions and open circles to the present work experimental values given in Table I. Up triangles are results of *ab initio* calculations of nucleic base anions. The solid square and the open diamonds correspond to photoelectron spectroscopy experimental determinations.

respectively. Another requirement is that parent molecules should be rotationally cold enough to obtain a sizable fraction with low J values able to give birth to stable anions. Finally the attachment process has to be efficient, involving very low energy attached electrons together with a stabilizing process. With respect to this point the Rydberg electron technique used here seems to be suitable. In a Rydberg atom, the external electron is prepared with a wave function somewhat similar to that of an electron in a dipole-bound anion. The involved collision then constitutes a charge exchange reaction into which the electron changes its attractive center still remaining in diffuse orbitals. Our measurements could be extended to larger Rydberg n values. However, a mass selection and detection scheme which is less perturbative should then be employed to extend the range towards lower anion binding energies.

From a theoretical point of view, dipole-bound anions constitute an interesting challenge as a test of *ab initio* techniques [4,5] for very diffuse outermost wave functions at an unusual degree of energy accuracy.

[1] M. Reed and B. Simon, *Methods in Modern Mathematical Physics* (Academic Press, San Diego, 1975).

[2] J.M. Levy-Leblond, Phys. Rev. **153**, 1 (1967), and references therein; O.H. Crawford, Proc. Phys. Soc. London **91**, 279 (1967).

[3] W.R. Garrett, Chem. Phys. Lett. **5**, 393 (1970); J. Chem. Phys. **69**, 2621 (1978); J. Chem. Phys. **77**, 3666 (1982).

[4] K.D. Jordan and P.D. Burrow, Acc. Chem. Res. **11**, 341 (1978); J. Simons and K.D. Jordan, Chem. Rev. **87**, 535 (1987).

[5] N. Oyler and L. Adamowicz, J. Phys. Chem. **97**, 11 122 (1993).

[6] O.H. Crawford, Mol. Phys. **20**, 585 (1971); O.H. Crawford and W.R. Garrett, J. Chem. Phys. **66**, 4968 (1977).

[7] K.R. Lykke, D.M. Neumark, T. Andersen, V.J. Trappa, and W.C. Lineberger, J. Chem. Phys. **87**, 6842 (1987).

[8] R.D. Mead, K.R. Lykke, and W.C. Lineberger, J. Chem. Phys. **81**, 4883 (1984); A.S. Mullin, K.K. Murray, C.P. Schulz, and W.C. Lineberger, J. Phys. Chem. **97**, 10 281 (1993).

[9] D.C. Clary, J. Phys. Chem. **92**, 3173 (1988).

[10] E.A. Brinkman, S. Berger, J. Marks, and J.I. Brauman, J. Phys. Chem. **99**, 7586 (1993).

[11] J.A. Stockdale, F.J. Davis, R.N. Compton, and C.E. Klots, J. Phys. Chem. **60**, 4279 (1974).

[12] T. Siugura and A. Arakawa, in *Proceedings of the International Conference on Mass Spectroscopy* (University of Tokyo Press, Tokyo, 1970).

[13] R. Hashemi and E. Illenberger, J. Phys. Chem. **95**, 6402 (1991).

[14] H. Haberland, H. Ludewigt, C. Schindler, and D.R. Worsnop, J. Chem. Phys. **81**, 3742 (1984).

[15] H. Haberland, H. Ludewigt, C. Schindler, and D.R. Worsnop, Phys. Rev. **36**, 967 (1987).

[16] C. Desfrançois, B. Baillon, J.P. Schermann, S.T. Arnold, J.H. Hendricks, and K.H. Bowen, Phys. Rev. Lett. **72**, 48 (1994).

[17] C. Desfrançois, H. Abdoul-Carime, C. Adjouri, N. Khelifa, and J.P. Schermann, Europhys. Lett. **26**, 25 (1994).

[18] C. Desfrançois, N. Khelifa, A. Lisfi, and J.P. Schermann, J. Chem. Phys. **96**, 5009 (1992).

[19] T. Kraft, M.W. Ruf, and H. Hotop, Z. Phys. D **14**, 179 (1989).

[20] D.R. Lide, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, 1993) 74th ed.

[21] H.S. Carman, C.E. Klots, and R.N. Compton, J. Chem. Phys. **90**, 2580 (1989).

[22] W.R. Garrett, J. Chem. Phys. **73**, 5721 (1980).

[23] T.M. Miller, D.G. Leopold, K.K. Murray, and W.C. Lineberger, J. Phys. Chem. **85**, 2368 (1986).

[24] H.W. Sarkas, J.H. Hendricks, S.T. Arnold, and K.H. Bowen, J. Chem. Phys. **100**, 1884 (1994).

[25] A. Oyler and L. Adamowicz (private communication).