Determination of electron binding energies of ground-state dipole-bound molecular anions

C. Desfrançois

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

(Received 22 December 1994)

We describe two simple models for the determination of electron binding energies (E_b) of several dipole-bound negative ions from field-detachment experiments and charge-transfer formation-rate-constant measurements in collisions between cold neutral molecules and Rydberg atoms. These models are able to correctly reproduce the experimental data, from which we deduce two compatible sets of E_b values. A curve-crossing model for calculating anion formation rate constants allows us to qualitatively understand the sharply peaked shapes of the experimental curves and to derive a simple quantitative law between E_b values and principal Rydberg quantum numbers at which anion formation rate constants are maximum.

I. INTRODUCTION

For a long time, it has been theoretically predicted that closed-shell molecules with high enough permanent electric-dipole moments are able to form stable negative ions [1,2]. In these dipole-bound anions, the extra electron is only bound by the long-range dipolar potential and its wave function is far more extended than usual molecular orbitals. The corresponding electron binding energies (E_b) are thus very low, most especially when the molecular dipole moment is just above the critical value for electron binding. The first experimental study, to our knowledge, on such stable ground-state dipole-bound anions for molecules whose dipole moments lie between 2.5 and 4 D has been recently reported [3]. Negative ions were efficiently produced by charge exchange between Rydberg atoms in nf states and cold molecules in a crossing-beam apparatus and a preliminary determination of the anion E_b values was made from electric-field detachment experiments. Moreover, the measured anion formation rate constants displayed unusual peaked n dependencies which were strongly correlated to E_b values.

The aim of the present work is to provide a quantitative interpretation of both field-detachment and rate-constant measurements in order to derive accurate E_b values for the whole set of dipole-bound negative ions studied. For such loosely bound negatively charged species, with a very outermost and extended electron orbital, *ab initio* calculations are very difficult [4] and, in fact, not more reliable than simpler models. In Sec. II, we thus derive the shape of the extra electron wave function, for a given E_b value, from an empirical dipolar potential and with the help of Clary's rotationally adiabatic theory, which has been proven to be quite accurate in that case [5]. This wave function is used in Sec. III where we develop a curve-crossing model for ion-pair formation [6], in order to fit experimental anion formation rate constants as a function of Rydberg quantum numbers n, and from which we obtain a first set of E_b values. In Sec. IV we simulate electric-field-detachment results with a sim-

ple formula previously derived by Smirnov and Chibisov for atomic negative ions [7] and then deduce a second independent set of E_b values. These two sets of results are compared and discussed in Sec. V.

II. DIPOLE-BOUND ANION WAVE FUNCTIONS

A great deal of theoretical work has already been devoted to the conditions into which an electron can be bound either in a pure dipolar potential [1] or in a more physical molecular dipole potential [2]. More recently, Clary developed an efficient theory in order to calculate energy levels and autodetachment widths of dipole-bound negative ions which has been successfully applied to excited radical anions [5]. Numerical results for E_b as a function of the molecular dipole moment have been previously reported [3] so that here we just recall the main calculation steps and focus on resulting electron wave functions.

We take the excess electron-molecule potential as the sum of dipolar, charge-induced dipole and short-range terms: $V(r,\theta) = V_\mu(r,\theta) + V_\alpha(r) + V_{SR}(r)$, where r, θ, and φ are the electron cylindrical coordinates with respect to the molecular symmetry axis. We shall consider the molecules studied as approximate symmetric tops so that the symmetry axis will almost be the same as the dipolar moment axis. V is expressed as (atomic units are used throughout this paper)

$$V_\mu(r,\theta) = \begin{cases} \dfrac{-\mu\cos(\theta)}{r^2} & \text{for } r > \mu/2 \\[2mm] \dfrac{-8r\cos(\theta)}{\mu^2} & \text{for } r < \mu/2 \ , \end{cases}$$

$$V_\alpha(r) = \frac{-\alpha}{2r^4} f(r) \ ,$$

where

$$f(r) = 1 - \exp[-(r/r_0)^6] \text{ and } r_0 = \alpha^{1/3} \ ,$$

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

TABLE I. Molecular and potential parameters used for calculating electron binding energies (E_b) and N values as described in Sec. II and corresponding to the best values of Table II for the fit of formation rate-constant measurements [3] as interpreted in Sec. III. μ and α values come from Ref. [9] and B values from Ref. [10], while r_c is the only adjustable parameter.

Molecule	μ (D)	B (cm^{-1})	α (Å^3)	r_c (a.u.)	N (a.u.)
Acetaldehyde	2.75	0.3213	4.6	3.55	0.183
Pivaldehyde	2.66	0.0918	10.0	4.11	0.214
Butanal	2.72	0.109	8.2	3.91	0.222
Cyclobutanone	2.89	0.1395	7.7	3.91	0.255
2-butanone	2.78	$\approx$0.1	8.1	3.84	0.252
Acetone	2.88	0.3116	6.4	3.54	0.286
Cyclopentanone	2.88	0.0961	9.3	3.93	0.297
TFMB	2.86	0.033	14.5	4.44	0.315
Cyclohexanone	2.87	0.071	11.5	3.98	0.352
Metacrylonitrile	3.69	0.1183	8.0	3.97	0.498
Acrylonitrile	3.87	0.12	8.05	4.14	0.519
Acetonitrile	3.924	0.3068	4.5	3.38	0.601

The first two terms vanish at short distance and only depend on the molecular dipole moment μ and polarizability α for which accurate experimental values are generally available (see Table I). On the contrary, the short-range term is somewhat arbitrary and will be adjusted in order to lead to a given E_b value. Since V_c and r_c are both nonindependent critical parameters for the resulting E_b, we set V_c equal to 1 a.u., keeping r_c as the only adjustable parameter. Following Clary's theory [5], we then calculate the lowest rotationally adiabatic potential $\varepsilon_{kJ}(r)$ after diagonalization of the Hamiltonian $H = B\vec{j}^2 + (A - B)\vec{j}_z^2 + \vec{l}^2/2r^2 + V(r,\theta)$, where $\vec{j}$ and $\vec{j}_z$ are the rotational angular-momentum operator of the molecule and its projection on the molecular symmetry axis, $\vec{l}$ is the relative orbital angular-momentum operator of the electron about the molecule, and J and k are the quantum numbers of the total angular momentum $\vec{J} = \vec{j} + \vec{l}$ and for $\vec{j}_z$. In agreement with the result established by Clary [5], it is

verified that the obtained $\varepsilon_{kJ}(r)$ are, for low r values, of the form $-A(r) + BJ(J+1) + (A-B)k^2$, where $A(r)$ is independent of J and k and only depends on B and the other molecular potential parameters. This is even better verified when large values of l are taken into account but this is practically true when considering only l values below four, indicating that the excess-electron angular momentum is essentially small in these dipole-bound systems. Energy levels E_{kJ} are obtained as solutions of the one-dimensional Schrödinger equation

$$\left[\frac{-1}{2} \frac{d^2}{dr^2} + \varepsilon_{kJ}(r) \right] R(r) = E_{kJ} R(r)$$

and are also of the form $-E_b + BJ(J+1) + (A-B)k^2$, where the electron binding energy E_b is also independent of J and k. Dipole-bound anions thus appear to have almost the same rotational energy levels as the isolated molecule, only shifted to lower energies by an amount equal to their electron binding energies [8]. E_b calculations are thus done with $J = k = 0$ and $l < 4$. In all cases studied, E_b values are low enough (<20 meV) so that there is only one ground-state bound energy level corresponding to a reduced radial wave function $R(r)$ with no node. Three of them, corresponding to three selected E_b values of Table II, are displayed in Fig. 1. Their asymptotic behavior for large electron-molecule distances is well expressed as

$$R(r) \underset{r \to \infty}{=} N \frac{e^{-\gamma r}}{r} \quad \text{where} \quad \gamma = \sqrt{2E_b} .$$

This is a typical behavior for distances larger than the potential range [6]. The corresponding normalization constants N are indicated in Table I and are used in the following sections.

The angular part of this wave function cannot be easily extracted from this model but it is mainly formed by low angular-momentum components as pointed out above and as has been shown by Clary [5]. Ab initio calculations [11] have also shown that the extra electron orbital is essentially a diffuse sp hybrid orbital that is positioned

TABLE II. Results for anion formation rate constants: n_{max} are the Rydberg quantum numbers at which experimental rate constants are maximum [3], V_i and R_c are the corresponding ionization potential and crossing radius, E_b and γ are the adjusted values that achieve the best fit of experimental data (see Fig. 3), and $k(n_{max}f)$ are the theoretical maximum formation rate constants.

| Molecule	n_{max}	$V_i(n_{max},f)$ (meV)	E_b (meV)	γR_c (a.u.)	$k(n_{max}f)$ (10^8 cm^3/s)
Acetaldehyde	41-42	8.1-7.7	0.70	19	14
Pivaldehyde	34	11.8	1.20	17	9.3
Butanal	33	12.5	1.29	17	9.3
Cyclobutanone	29	16.2	1.88	16	7.2
2-butanone	28-29	17.4-16.2	1.89	15	7.5
Acetone	24-25	23.6-21.8	2.97	14	5.5
Cyclopenatanone	24	23.6	3.18	14	5.5
TFMB	22-23	28.1-25.7	3.73	14	4.6
Cyclohexanone	19	37.7	5.78	12	3.8
Metacrylonitrile	15-16	60.5-53.1	10.8	12	2.5
Acrylonitrile	15-16	60.5-53.1	10.8	12	2.5
Acetonitrile	13	80.5	18.6	11	1.6
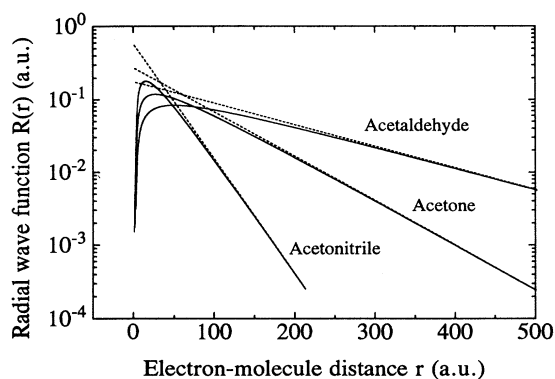
FIG. 1. Radial wave function of acetonitrile, acetone, and acetaldehyde dipole-bound anions. The dotted curves are their asymptotic behavior for large electron-molecule distances r and are equal to the normalization constant N for $r = 0$, as defined in the text.

only slightly away from the molecular frame in the direction of the molecular dipole. In the following, we shall thus consider the angular part of the wave function $Y(\theta, \varphi)$ as a superposition of an s orbital together with a p orbital oriented along the dipole-moment axis,

$$Y(\theta, \varphi) = \frac{1}{\sqrt{2}}(Y_0^0 + Y_1^0) \ .$$

III. ELECTRON BINDING ENERGIES FROM EXPERIMENTAL ANION FORMATION RATE CONSTANTS

Dipole-bound anions have been created in charge-exchange collisions between neutral rotationally cooled molecules and xenon Rydberg atoms laser excited in states nf [3]. Formation rate constants for this process have been shown to be strongly dependent upon the principal quantum number n and upon E_b. Large E_b values correspond to small quantum numbers n_{max} at which rate constants are maximum while low E_b values correspond to n_{max} as large as 40. Such a sharp sensitivity has also been observed in atomic calcium negative-ion formation produced by similar charge-exchange collisions between calcium atoms in ground states and Rydberg states [12]. It has been interpreted, within the impulse approximation, as a resonant energy transfer when the ionization potential of the Rydberg atom is almost equal to the electron binding energy of the created calcium negative ion [13]. As it can be seen in Table I, E_b values are in the present case always much lower than the ionization potential corresponding to n_{max} so that the observed process is always endothermic. The same model cannot hold here but such charge-exchange reactions are also often well understood in terms of curve-crossing models as developed below.

As displayed in Fig. 2, flat covalent diabatic potential curves, corresponding to neutral xenon atoms in nl Rydberg states plus neutral polar molecules, cross ionic Coulombic diabatic curves, corresponding to ion pairs
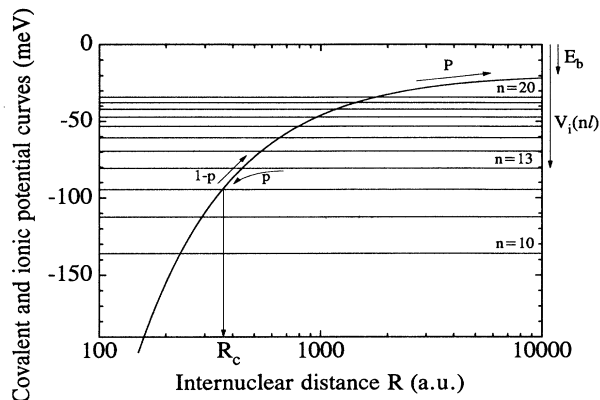

FIG. 2. Covalent potential curves corresponding to $Xe(nl) + M$ and ionic potential curve corresponding to $Xe^+ + M^-$ as a function of the internuclear distance R, for a zero impact parameter b. At each crossing radius R_c the ionic-covalent coupling term $H_{ic}(R_c)$ can make the system pass from one curve to the other with a probability p. P is the resulting ion-pair formation probability.

$Xe^+ + M^-$. Charge exchange is supposed to occur without any change in the molecular geometry and internal state since the extra electron takes place in a very diffuse outermost orbital. We thus assume the same molecular rovibrational internal state for the neutral molecule and the created anion and only consider one ionic diabatic curve corresponding to the single ground anion electronic state. Since the equilibrium internuclear distances of the anions and their neutral parents are very similar, we shall also consider that adiabatic and vertical electron affinities (A_e) are both equal to E_b, whatever the considered internal rovibrational state. Covalent curves cross ionic curves at internuclear distances R_c which only depend on Rydberg ionization potentials $V_i(nl)$ and E_b:

$$R_c(nl) \approx \frac{1}{V_i(nl) - E_b}$$

with

$$A_e^{ad} \approx A_e^{vert} \simeq E_b$$

At each diabatic crossing, the Hamiltonian interaction term $H_{ic}(R_c)$ can make the system pass from one potential curve to the other one with an adiabatic probability p which is here calculated with the following simplified Landau-Zener expression [14,15]:

$$p(nl, R_c, b) = 1 - \exp\left[\frac{-2\pi H_{ic}^2 R_c^2}{v_r}\right] ,$$

where

$$v_r = \sqrt{2/m[E - V(R_c) - \varepsilon(b^2/R_c^2)]} ,$$

v_r is the radial velocity at R_c for the impact parameter b and for the system with a reduced mass m, an initial kinetic energy ε, total energy E, and a potential energy $V(R_c) \approx V_i(nl)$. Starting from an initial selected Rydberg

$n_0 f$ state, it is easy to compute the total probability P for ion-pair formation after passing across the crossing network and the corresponding anion formation rate constant k after summing P over impact parameters b,

$$P(b) = p(n_0 f)(1 - p(n_0 f))$$

$$\times \left[\prod_{V_i(nl) < V_i(n_0 f)}^{nl} (1 - p(nl)) \right]$$

$$\times \left[1 + \sum_{V_i(n_0 f) < V_i(nl)}^{nl} p^2(nl) \right.$$

$$\times \left. \prod_{V_i(n_0 f) < V_i(n'l') < V_i(nl)}^{n'l'} (1 - p(n'l'))^2 \right]$$

$$k(n_0 f) = 2\pi v \int_0^{R_c(n_0 f)} P(b) b \, db \quad \text{with} \quad v = \sqrt{(2/m)\varepsilon} \ .$$

It can be seen from these expressions why we obtain peaked curves for $k(n_0)$. Since P is mainly determined by the first factor $p(n_0)(1 - p(n_0))$, and because p is strongly dependent upon the Rydberg state nl and its crossing radius, k will be maximum for the initial Rydberg state $n_{\max} f$ for which p will be as close as possible to $1/2$. For low impact parameters, this condition implies

$$H_{ic}^2 R_c^2 \approx \frac{\ln(2)}{2\pi} v$$

where

$$R_c = \frac{1}{V_i(n_{\max} f) - E_b}$$

and

$$V_i(n_{\max} f) \approx \frac{1}{2 n_{\max}^2} \ .$$

As described below, the ionic-covalent coupling term $H_{ic}(R_c)$ is a strongly decreasing function of R_c and a much less strongly increasing function of n so that lower E_b values will correspond to lower $V_i(nl)$ and larger $n_{\max}$ values in order to still satisfy the above condition.

In order to get accurate results, the most critical step in such models is to correctly evaluate the ionic-covalent coupling term. An expression has been derived by Janev [16] which has also been proven to be quite accurate for the interpretation of charge-transfer collisions between excited rubidium atoms [17]. If l and l' are the quantum numbers for the electron orbital angular momentum, respectively, in the Rydberg atom and the dipole-bound ion, and if m is their common projection on the internuclear axis, the ionic-covalent coupling term can be expressed as

$$H_{ic}(R_c) = \frac{NL}{2(2\gamma R_c)^{|m|}|m|!} \chi_{nl}(R_c)$$

where

$$L = \sqrt{(2l+1)(2l'+1)[(l+|m|)!(l'+|m|)!/(l-|m|)!(l'-|m|)!]} \ .$$

In this expression N is the anion orbital normalization constant as defined in Sec. II, $\gamma = \sqrt{2E_b}$, and χ_{nl} is the radial wave function of the considered nl Rydberg state. It is valid only in the asymptotic limit of large crossing radius, namely for $\gamma R_c \gg 1$. As can be seen in Table II, this condition is quite well fulfilled in the present study. The angular part $Y(\theta, \varphi)$ of the anion orbital is considered as an sp hybrid orbital oriented along the dipole moment axis. It can be expressed in terms of spherical harmonics in the internuclear frame for which the internuclear axis becomes the z axis, as a function of the Euler angle β between the dipole moment axis and the internuclear axis when charge exchange occurs,

$$Y(\theta', \varphi') = \frac{1}{\sqrt{2}} \left[Y_0^0 + \cos(\beta) Y_1^0 + \frac{\sin(\beta)}{\sqrt{2}} (Y_1^1 - Y_1^{-1}) \right] \ .$$

We then deduce the expressions of the coupling term as a function of the quantum number m for the projection on the internuclear axis of the orbital angular momentum for an electron in a Rydberg state n, l, m and as a function of β,

$$H_{ic}(n, l, 0) = \frac{N\sqrt{2l+1}}{2\sqrt{2}} [1 + \sqrt{3}\cos(\beta)] \chi_{nl}(R_c) \ ,$$

$$H_{ic}(n, l, \pm 1) = \frac{N\sqrt{6l(l+1)(2l+1)}}{8\gamma R_c} \sin(\beta) \chi_{nl}(R_c) \ ,$$

$$H_{ic}(n, l, |m| > 1) = 0 \ .$$

The probability for ion-pair formation depends on β and has to be averaged before integrating over impact parameters [15,18]: $P(b) = \frac{1}{2} \int_0^\pi P(b, \beta) \sin(\beta) d\beta$. Even if the two above expressions for $m = 0$ and $|m| = 1$ seem to be rather different, the critical term is the radial Rydberg wave function $\chi_{nl}(R_c)$ in both cases. Calculations are thus not very sensitive to the shape of the anion orbital: we also made calculations with a simplified expression for $H_{ic}(R_c)$, considering that the angular part of the orbital is a pure s orbital. The ionic-covalent coupling term is then independent of β,

$$H_{ic}(n, l, 0) = \frac{N\sqrt{2l+1}}{2} \chi_{nl}(R_c)$$

and

$$H_{ic}(n, l, |m| > 0) = 0 \ .$$

Results for these two sets of calculations are displayed in Table II and Fig. 3. In both cases, we take into account a large umber of covalent nlm states (up to more than 1000) in order to get convergent values for the rate constants. Since in the experiments molecules are seeded in helium, the kinetic energy ε is always large enough to allow for ion pairs to dissociate [19], namely $\varepsilon > V_i(nl) - E_b$. As in the preceding section, we look for the potential parameter r_c and the corresponding E_b value that provide the best fits between calculated and ex-

perimental anion formation rate constants as a function of the Rydberg principal quantum number n. Both expressions for H_{ic} lead to the same optimal E_b values and almost the same shape for the rate-constant curves as illustrated in Fig. 3. The only noticeable difference is that the angular independent expression leads to rate constants higher than those indicated in Table II by a factor of about 1.5.

IV. ELECTRON BINDING ENERGIES FROM ELECTRIC-FIELD DETACHMENT EXPERIMENTS

Electron binding energies of anions are usually experimentally determined with great accuracy by means of photodetachment techniques [8,20]. However, these techniques require rather large anion intensities which, up until now, have not been obtained for dipole-bound
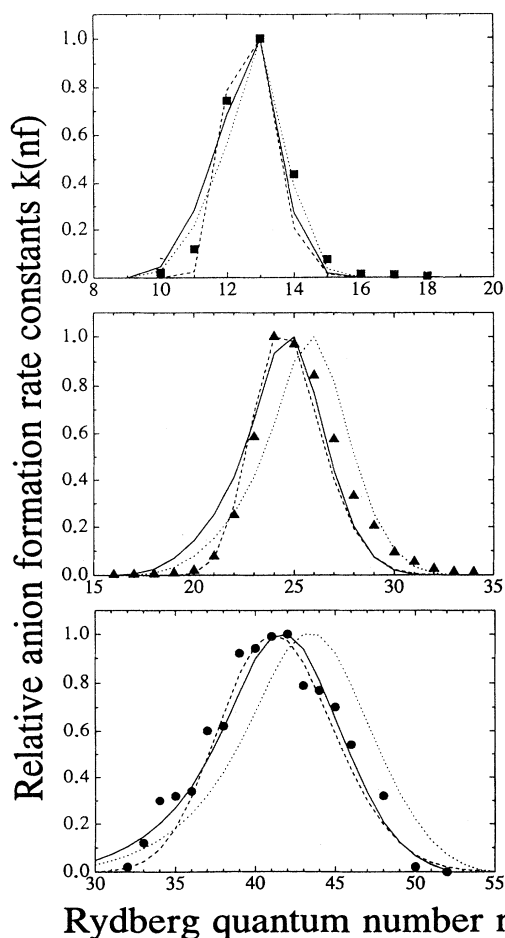

FIG. 3. Experimental and theoretical fitted curves for the relative formation rate constants of acetonitrile (squares), acetone (triangles), and acetaldehyde (circles) dipole-bound anions created in charge-transfer collisions with Rydberg states nf. Full and dotted curves correspond to calculations done with the β-dependent ionic-covalent coupling term (see text) and respective E_b values of Table II and Table III. The dashed curves are obtained with the angular independent coupling term and the same E_b values of Table II.

anions. Fortunately, for these weakly bound anions, E_b values range in the thermal and subthermal domains and excess electrons can then be detached by applying external electric fields of the order of some tens of kV/cm [3,21]. In Ref. [3], estimates for the E_b values of the twelve molecules studied have been derived by fitting the experimental field-detachment probably curves by the transmission factor of the potential barrier between a pure dipolar potential $-\mu/r^2$ and an electrostatic potential $-Fr$ corresponding to a static electric field F antiparallel to the molecular dipole moment, at an energy equal to E_b. The detachment probability was then assumed to be equal to one only when the top of the barrier was lowered to the E_b value, i.e., when the electric field reached the critical value F_c defined by $27\mu F_c^2 = E_b^3$. The obtained values were then most probably underestimated since an extra electron encounters this barrier many times during the period of time where the ion is submitted to the field, which is much larger (few tens of ns) than the electronic period (less than a ps).

A first improvement can be obtained by simply multiplying the transmission factor $T(F)$ by the classical frequency of the electron orbital motion $v(E_b)$ in order to get the probability per unit of time $\omega(F, E_b)$ for field detachment. These quantities can be calculated as follows:

$$T(F) = \exp(-C)$$

with

$$C = 2 \int_{r_1}^{r_2} \sqrt{2(\varepsilon_{kJ}(r) - E_b)} \, dr \ ,$$

$$v(E_b) = \frac{1}{T_c} \ ,$$

where

$$T_c = 2 \int_{r_0}^{r_1} \frac{dr}{\sqrt{2[E_b - \varepsilon_{kJ}(r)]}} \ ,$$

$$\omega(F, E_b) = v(E_b) T(F) \ ,$$

where r_0, r_1, and r_2 are the classical turning points for the energy $-E_b$ on the rotationally adiabatic surface $\varepsilon_{kJ}(r)$ calculated as in Sec. II but with an electron-molecule potential that contains an additional electrostatic potential term: for an electric field antiparallel to the dipole moment, the field potential is indeed expressed as $-Fr\cos(\theta)$ and can thus be treated in the same way as the dipolar potential term. The prefactor v in this expression is, however, only a crude classical estimate and we still suppose that the field-detachment process always occurs when the dipole moment is antiparallel to the electric field. For the present electric-field values (≤ 10 kV/cm) and the polar molecules here considered ($\mu \approx 2$–4 D) the maximum electrostatic potential energy of such dipoles remains small (< 0.1 meV) compared to the mean rotational kinetic energy of the crated anions which is of the same order as their neutral parents (≈ 1 meV for a rotational temperature in the beam of about 10 K). Rotational distributions will thus remain mainly unchanged by the presence of the field. Since rotational periods (several tens of ps) are much shorter than the

anion time of flight in the detaching field region (several tens of ns), a proper treatment must take into account all the possible orientations between the dipole moment and the electric field.

We thus use an expression previously established by Smirnov and Chibisov [7] which has been proven to be rather accurate for the highest bound states of several atomic negative ions whose E_b values are of the same order as those considered here [21]. Even if it has been used only for spherical electron-atom potentials, this expression can be still quite accurate in the present case since it has been established for an electron loosely bound in a short-range potential well of arbitrary shape with a given orbital angular momentum l, under the only assumption that the electric field F is low enough, namely, if $F \ll (2E_b)^{3/2} = \gamma^3$. This condition is well fulfilled for the present experimental critical electric fields (see Table II). The probability per unit of time $\omega_{l,m}$ is then given by

$$\omega_{l,m}(F,E_b) = \frac{N^2(2l+1)}{4\gamma^{|m|}} \frac{|m|!(l-|m|)!}{(l+|m|)!}$$
$$\times \left[\frac{F}{\gamma^2} \right]^{|m|+1} \exp\left[-\frac{2\gamma^3}{3F} \right],$$

where γ and N have been defined in the preceding section and l, m are the quantum numbers for the extra electron orbital angular momentum and its projection along the electric-field axis. Using the same frame transformation for the angular part of the anion wave function as in the preceding section, where β is now the Euler angle between the dipole moment axis and the field axis, we deduce the expression of ω as function of β,

$$\omega_\beta(F,E_b) = \frac{\omega_{0,0}}{2} + \frac{\cos^2(\beta)}{2}\omega_{1,0} + \sin^2(\beta)\omega_{1,1}$$
$$= \omega_{0,0}\left[\frac{1+3\cos^2(\beta)}{2} + \frac{3F}{4\gamma^3}\sin^2(\beta) \right].$$

Averaging over all β values, the mean decay probability
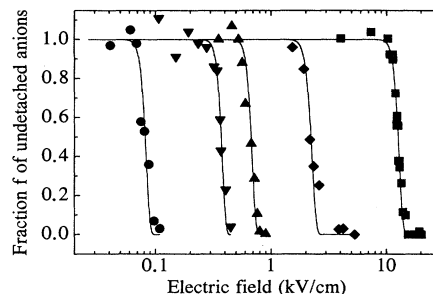

FIG. 4. Experimental field-detachment curves for acetaldehyde (circles), cyclobutanone (down triangles), acetone (up triangles), cyclobutanone (diamonds), and acetonitrile (squares) together with the fitted theoretical curves calculated with Smirnov's formula (see text) and corresponding to E_b values of Table III.

$\bar{\omega}$ then reduces to $\omega_{0,0}$,

$$\bar{\omega}(F,E_b) = \tfrac{1}{2}\int_0^\pi \omega_\beta \sin(\beta)d\beta \approx \omega_{0,0} = \frac{N^2F}{4\gamma^2}\exp\left[-\frac{2\gamma^3}{3F} \right],$$

since

$$F \ll \gamma^3 .$$

The experimental measured quantity is the fraction f of dipole-bound anions that have not been field detached after passing through the detaching electric-field region during a time T. In our calculations we assume that the electric field is uniform in this region so that f is easily derived from $\bar{\omega}$ as $f(F,E_b,T) = \exp(-\bar{\omega}(F,E_b)T)$. T is a known experimental parameter (see Table III) and the experimental field dependency of f can be fitted by varying E_b which depends on the single adjustable parameter r_c as described in Sec. II. Such fits are displayed in Fig. 4 for some selected anions, using the above expression of Smirnov and Chibisov for ω and leading to E_b values as indicated in Table III. The other expression leads to very similar E_b values which are only lower by less than 15%

TABLE III. Results for electric-field detachment when using the formula of Smirnov and Chibisov [7]. F_c is the critical electric field above which one half of the anions detach after a time T in the experimental conditions [3]. r_c, E_b, and γ are the adjusted values that achieve the best fit of experimental data (see Fig. 4).

Molecule	F_c (kV/cm)	T (ns)	r_c (a.u.)	E_b (meV)	γ^3/F_c (a.u.)
Acetaldehyde	0.080	2020	3.58	0.63	20.3
Pivaldehyde	0.122	2490	4.23	0.83	20.1
Butanal	0.182	2000	3.97	1.07	19.7
Cyclobutanone	0.370	1480	3.93	1.78	20.8
2-butanone	0.390	1480	3.85	1.82	20.4
Acetone	0.673	1050	3.57	2.65	20.8
Cyclopentanone	0.791	1150	3.95	2.97	21
TFMB	1.185	1260	4.41	3.98	21.7
Cyclohexanone	1.92	70	4.01	5.27	20.4
Metacrylonitrile	4.95	58	3.99	10.5	22.3
Acrylonitrile	5.76	52	4.20	10.8	20
Acetonitrile	12.0	45	3.40	18.0	20.6

and with the same quality of fits. As compared to the previously reported estimates [3] the present values are larger by a factor of 1.5 for the largest E_b values up to 1.9 for the lowest ones. A more refined treatment of atomic negative-ion decay in an external field has been recently developed by Fabrikant [22]. It takes into account the long-range part of the electron-atom interaction leading to larger field-detachment probability values ω. It is unclear how important this long-range contribution would be in the present case but it should also increase ω, leading to even larger E_b values. Due to the anisotropy of the dipolar potential, the increase may be, however, smaller than in the case of isotropic polarization potentials. The values obtained E_b are somewhat lower than those derived in the previous sections (Table II) except for the trifluoromethylbenzene (TFMB) molecule. The difference is generally, however, of the order of 10%, except for two low E_b values corresponding to pivaldehyde (33%) and butanal (20%) molecules while the agreement is very good for the three largest E_b values ($< 5\%$).

V. DISCUSSION

We first want to discuss the precision of the above reported electron binding energies. The first set of E_b values, deduced from rate-constant measurements, should be more reliable since the main sources of uncertainties do not affect theoretical results. As shown in Sec. III, results depend weakly on the shape of the dipole-bound wave function. For high principal Rydberg quantum numbers n, the initial orbital quantum number l may experimentally be different from three due to l-mixing collisions on the carrier gas (He) and for low n values blackbody radiations may also induce some l mixing [19]. The theoretical n dependency of anion formation rate constants is, however, weakly dependent upon initial l values that only affect the absolute rate constant values. The maximum rate constant value reported here for acetonitrile anion formation at $n = 13$ (1.6×10^{-8} cm^3/s) is, however, in good agreement with the experimental estimate ($\approx 10^{-8}$ cm^3/s [23]). This simple curve-crossing model is thus able to reproduce both n dependencies and absolute values for the formation rate constants so that the deduced E_b values should be accurate within a precision of 10%, at least for the largest values. The second set of values, deduced from field-detachment experiments, suffers mainly from two kinds of systematic errors: electric-field values may have been overestimated by about 10% since voltages were applied to plates or grids whose holes or mesh were only three or four times less than the distance between them. On the other hand, as quoted above, the expression we use for the field-detachment probabilities may be underestimated and it is unclear whether or not these two errors compensate.

Another important point is that in both above models, we forgot about initial and final rotational states and possible rotational energy exchanges during the attachment and detachment processes. For an estimated rotational temperature of 10 K [3] in the neutral molecular beam, the mean rotational kinetic energy is of the order of 1

meV and the mean j and k values for the rotational angular momentum of the order of a few units. For the experimentally observed dipole-bound anions, J and K must verify $BJ(J+1)+(A-B)K^2 < E_b$ otherwise their autodetachment lifetimes become much less than the experimental time scale [5,8]. This condition is not too restrictive for large E_b values such as for acetonitrile ($J < 22$ for $K = 0$) but becomes important for low E_b values such as for acetaldehyde ($J < 4$ for $K = 0$). In that case, the above-reported absolute formation rate constant values may be larger than experimental ones since part of the created anions may have rapidly autodetached before acceleration and detection. Since the extra electron orbital momentum in the dipole-bound wave function is small, we assume that, during the attachment or detachment process, $J \approx j$ and $K \approx k$ so that we really measure the actual E_b value. If some rotational energy exchange $\Delta E_{\rm rot}$ occurs, we then measure $E_b \pm \Delta E_{\rm rot}$. For $|J - j| < 2$, $\Delta E_{\rm rot}$ remains smaller than 0.5 meV, i.e., much lower than the largest determined E_b values. On the contrary, the discrepancy between the two sets of low E_b values may come from such small but non-negligible rotational energy exchanges.

For molecules with a dipole moment lower than 5 D, only a few ab initio calculations have been done by Jordan and co-workers [4] on some small polar molecules and by Oyler and Adamowicz on biological molecules [11] and on the molecules studied here [24]. Calculated electron affinity values obtained in the Koopman's theorem approach appear to be lower than those reported here by a factor larger than 2, despite calculated dipole moments larger than experimental measurements [9]. Such low E_b values seem to be still below the limit of precision for ab initio methods. On the contrary, earlier simple pseudopotential calculations by Garrett [2] often overestimate E_b by a factor larger than 2 because of the lack of experimental data at that time in order to adjust the empirical parameters, especially for the repulsive part of the electron-molecule potential. Using the generalized quantum-defect theory together with experimental electron-scattering data, Fabrikant also reported some electron affinities of dipole-bound molecular anions [25]. He predicted a value of 1.6 meV for cyclopentanone and of 72 meV for 1-butyronitrile. The first value is lower than the one here reported although it has been calculated with a dipole moment value of 3.3 D which is probably largely overestimated as compared to the more reliable measurements for cyclobutanone and cyclohexanone [9]. The second value seems to be large as compared to our value for acetonitrile whose dipole moment, polarizability, and structure are similar.

As discussed above, accurate E_b values for such loosely bound dipole-bound negative ions are difficult to determine even with the help of experimental data. The Rydberg electron transfer technique together with a simple theoretical model seems to be the most accurate method as in the case of atomic negative ions [12,13]. This is illustrated in Fig. 5 where E_b values of Table I are plotted as a function of the principal quantum number $n_{\rm max}$ at which formation rate constants are maximum. It is clear-
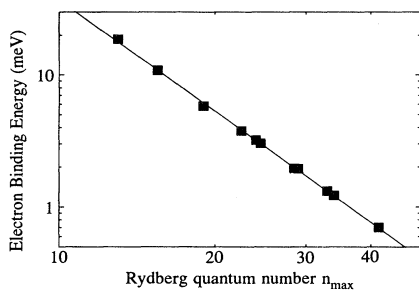
FIG. 5. Optimal electron binding energies of the twelve molecules studied as a function of the principal Rydberg quantum number n_{max} at which dipole-bound anion formation rate constants are maximum (from Table II). The straight line is a least-square fit as defined in the text.

ly seen that a simple power law links these two quantities with a precision better than 5%,

$$E_b = \frac{22\,910 \text{ meV}}{n_{max}^{2.793}} \cdot$$

It is unclear, from the above curve-crossing calculations, where this law does come from but it may, however, be useful for direct E_b determination from Rydberg electron transfer rate-constant measurements. As an example, we recently measured formation rate constants for thymine dipole-bound anions and determined $n_{max} = 8$ [26]. According to the above power law, this leads to $E_b \approx 70$ meV to be compared to the predicted ab initio values of 88 meV [11]. Field-detachment experiments are in progress in order to ascertain the above experimental value.

VI. CONCLUSION

So far, two different models were mostly considered for describing inelastic and charge-exchange collisions between excited atoms A^* and ground-state atoms or molecules X. On one hand, the impulse approximation [27], developed for highly excited atoms A^{**}, allows the treatment of the collisional process as a two-body interaction $e + X$ between the excited atom outer electron and its col-

liding partner. The role of the atomic positive core A^+ is then only to prepare the quantum distribution of the electron in momentum space. On the other hand, for moderately excited atoms, several curve-crossing models [6,15,18] consider the interaction between the whole ionic $A^+ + X^-$ and covalent $A^* + X$ configurations as a real three-body problem.

Recently, two experiments demonstrated very sharp dependences of the ion-pair formation cross sections as a function of the principal quantum number n of highly excited Rydberg atoms $A^{**}(nl)$. The production of Ca^- negative ions resulting from collisions between $Ca^{**}(nd)$ and $Ca(4s^2)$ only for $n = 25$ [12] has been interpreted within the framework of the impulse approximation [13]. The energy transfer between the translational nuclear motion and the electron motion must be very weak (much less than the mean kinetic energy of the Rydberg electron), leading to a sharply resonant process, since the exchanged Rydberg electron momentum is much smaller than the relative collision momentum. In the present work the maxima of ion-pair formation rate constants occur for Rydberg states whose ionization potentials $V_i(nl)$ are always much larger than the corresponding E_b values leading to an energy transfer of the order of V_i. This cannot be taken into account by an inelastic collision between a quasifree Rydberg electron and the molecule. During the collision process the positive ionic core A^+ must also interact with the nascent dipole-bound anion in order to satisfy energy conservation.

There is thus no contradiction between these two different models: impulse approximation or quasifree electron models are suitable for quasiresonant processes which are generally the case when highly excited Rydberg states are involved. When the energy exchange is of the same order as the mean Rydberg electron energy $\langle V_i \rangle$ curve-crossing models must be used even for high excited Rydberg states. One should thus compare the collision exchange energy and the Rydberg ionization potential, more than V_i alone, before employing one description or another. This is probably the reason for the rather surprising success of the ionic-covalent model developed here even for unusually large Rydberg quantum numbers n up to 40.

[1] E. Fermi and E. Teller, Phys. Rev. 72, 399 (1947); J. M. Levy-Leblond, Phys. Rev. 153, 1 (1967).

[2] O. H. Crawford, Mol. Phys. 20, 585 (1970); W. R. Garrett, J. Chem. Phys. 69, 2621 (1978).

[3] C. Desfrançois, H. Abdoul-Carime, N. Khelifa, and J. P. Schermann, Phys. Rev. Lett. 73, 2436 (1994).

[4] J. Simons and K. D. Jordan, Chem. Rev. 87, 535 (1987); K. D. Jordan and J. J. Wendoloski, Chem. Phys. 21, 145 (1977).

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

[6] R. Grice and D. R. Herschbach, Mol. Phys. 27, 159 (1974).

[7] B. M. Smirnov and M. I. Chibisov, Zh. Eksp. Teor. Fiz. 49, 841 (1966) [Sov. Phys. JETP 22, 585 (1966)]; Yu. N.

Demkov and G. F. Drukarev, ibid. 81, 1218 (1981) [54, 650 (1981)].

[8] R. D. Mead, K. R. Lykke, and W. C. Lineberger, J. Chem. Phys. 81, 4883 (1984).

[9] Handbook of Chemistry and Physics, 74th ed. (CRC, Boca Raton, 1993); G. Herzberg, in Electronic Spectra of Polyatomic Molecules (Van Nostrand Reinhold, New York, 1966).

[10] Numerical Data and Functional Relationships in Science and Technology, edited by K. H. Hellwege and A. M. Hellwege, Landolt-Börnstein, New Series, Group II, Vols. 4 and 6 (Springer-Verlag, Berlin, 1974).

[11] N. A. Oyler and L. Adamovicz, J. Phys. Chem. 97, 11 122 (1993); Chem. Phys. Lett. 219, 223 (1994).

[12] K. W. McLaughlin and D. W. Duquette, Phys. Rev. Lett. **72**, 1176 (1994).

[13] I. I. Fabrikant, Phys. Rev. A **48**, R3411 (1993), and references therein.

[14] E. E. Nikitin, *Theory of Elementary Atomic and Molecular Processes in Gases* (Clarendon, Oxford, 1974), and references therein.

[15] C. Desfrançois, J. P. Astruc, R. Barbe, and J. P. Schermann, J. Chem. Phys. **88**, 3037 (1988).

[16] R. K. Janev, J. Phys. B **4**, 215 (1971); J. Chem. Phys. **64**, 1891 (1976); R. K. Janev and A. Salin, J. Phys. B **5**, 177 (1972); M. I. Chibisov and R. K. Janev, Phys. Rep. **166**, 1 (1988).

[17] L. Barbier, M. T. Djerad, and M. Cheret, Phys. Rev. A **34**, 2710 ((1986).

[18] E. A. Gislason and J. G. Sachs, J. Chem. Phys. **62**, 2678 (1975).

[19] T. Kraft, M. W. Ruf, and H. Hotop, Z. Phys. D **14**, 179 (1989); C. Desfrançois, A. Lisfi, and J. P. Schermann, Z.

Phys. D **24**, 297 (1992).

[20] J. V. Coe, J. G. Eaton, S. T. Arnold, H. W. Sarkas, K. H. Bowen, C. Ludewigt, H. Haberland, and D. R. Worsnop, J. Chem. Phys. **92**, 3980 (1990).

[21] V. A. Oparin, R. N. Il'in, I. T. Sernkov, and E. S. Solov'ev, Zh. Eksp. Teor. Fiz. **66**, 2008 (1974) [Sov. Phys. JETP **39**, 989 (1974)].

[22] I. I. Fabrikant, J. Phys. B **26**, 2533 (1993).

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

[24] G. L. Gutsev, A. L. Sobolewski, and L. Adamovicz (private communications).

[25] I. I. Fabrikant, J. Phys. B **16**, 1253 (1983).

[26] H. Abdoul-Carime, C. P. Schultz, C. Desfrançois, and J. P. Schermann (to be published).

[27] M. Matsuzawa, J. Phys. B **8**, 2114 (1975); L. Petitjean, F. Gounand, and P. R. Fournier, Phys. Rev. A **30**, 736 (1984).