Comment on "Electron affinities from endothermic negative-ion charge-transfer reactions. IV. SF6, selected fluorocarbons and other polyatomic molecules"

C. Lifshitz, T. O. Tiernan, and B. M. Hughes

Articles you may be interested in

Femtochemistry of mass-selected negative-ion clusters of dioxygen: Charge-transfer and solvation dynamics
J. Chem. Phys. **115**, 612 (2001); 10.1063/1.1384549

Negative ion chemistry and the electron affinity of SF6
J. Chem. Phys. **77**, 826 (1982); 10.1063/1.443898

Electron affinities from endothermic negative-ion charge-transfer reactions. IV. SF6, selected fluorocarbons and other polyatomic molecules
J. Chem. Phys. **59**, 3182 (1973); 10.1063/1.1680459

Electron affinities from endothermic negative-ion charge-transfer reactions. III. NO, NO2, SO2, CS2, Cl2, Br2, I2, and C2H
J. Chem. Phys. **59**, 3162 (1973); 10.1063/1.1680458

Electron Affinities from Endothermic Negative-Ion Charge-Transfer Reactions. II. O2
J. Chem. Phys. **55**, 5692 (1971); 10.1063/1.1675740

upon expanding the quantum expression by introducing intermediate sums over states, matrix elements $x_{n,n'}$ enter and the identification in Eq. (3) results.

Milloni's second point concerns my statement that absorption and induced emission balance each other in the completely classical ($\hbar \to 0$) limit. This is so clear and well known[3] that it hardly needs comment. The quantum expression for the net energy absorbed, for example, involves the imaginary part of the dipole correlation function, which is indeed nonzero quantum mechanically. Classically, however, the dipole correlation function is real and there is no *net* energy change. For the case of a Boltzmann distribution over molecular states it is possible to express the imaginary part of the dipole correlation function in terms of the real part,[3] but here too the imaginary part vanishes as $\hbar \to 0$ (which is the standard way one always obtains the classical limit of quantum mechanics.[4])

Finally, Milonni notes (cf. end of third paragraph) that over the years there have been "long standing debates over whether the quantum theory of radiation is required to properly describe the observed features of spontaneous emission." This was the reason, of course, I thought it interesting in Ref. 1 to point out how simply spontaneous emission appears in the classical model developed there. (The comments on spontaneous emission are mentioned only as an aside.) The basic reason the picture is so simple is that both molecule and radiation field are treated on the same dynamical foot-

ing, i.e., both by classical mechanics: Spontaneous emission is simply energy transfer between two coupled oscillators, the "molecule oscillator" which is initially excited and the "radiation field oscillator" that is initially unexcited. Classical mechanics is, of course, only an approximation to quantum mechanics, so the spontaneous emission rates computed from the classical formulas—i.e., by using the classical dipole correlation function—will not in general give the exactly correct quantum values. (If the molecule is a harmonic oscillator, though, the classical result happens to be exact.) The point is that the process is described qualitatively correctly, and for molecular systems the description is even often quantitative.

ACKNOWLEDGMENTS

[1]W. H. Miller, J. Chem. Phys. **69**, 2188 (1978).
[2]See, for example, W. H. Miller, and C. W. McCurdy, J. Chem. Phys. **69**, 5163 (1979).
[3]See, for example, R. G. Gordon, Adv. Magn. Reson. **3**, 1 (1968).
[4]Cf. W. H. Miller, Adv. Chem. Phys. **25**, 69 (1974).

Comment on "Electron affinities from endothermic negative-ion charge-transfer reactions. IV. SF₆, selected fluorocarbons and other polyatomic molecules"

C. Lifshitz

Department of Physical Chemistry, The Hebrew University of Jerusalem, Israel

T.O. Tiernan

Brehm Laboratory and Department of Chemistry, Wright State University, Dayton, Ohio 45435

B.M. Hughes

Gulf South Research Institute, New Orleans, Louisiana
(Received 8 August 1979; accepted 12 September 1979)

Determinations of energy thresholds for the dissociative electron transfer processes,

$$X^- + SF_6 \to SF_5^- + F + X \qquad (1)$$

where $X = O$, S, F, Br and I, were made several years ago.[1] The electron affinity of the SF_5 radical was deduced from these measurements to be E. A. $(SF_5) \geq 2.8 \pm 0.1$ eV. This evaluation was based on a calculation which involved the bond dissociation energy $D_0(F_5S-F)$ of neutral SF_6,

$$E. A. (SF_5) = E. A. (X) + D_0(F_5S-F) - \Delta H_{R1} \qquad (2)$$

where ΔH_{R1} is the measured energy threshold and E. A. (X) is the electron affinity of the atomic reactant. The value employed for the bond dissociation energy of SF_6 at that time was given by Cottrell,[2] as $D_0(F_5S-F) = 3.3$ eV. This bond energy value is very close to the one quoted by Hildenbrand,[3] on the basis of the threshold energy of formation of F^- from SF_6. However, Kiang, Estler, and Zare have determined recently[4] new accu-

rate upper and lower bounds on the F_5S-F bond energy,

$$D_0^o(F_5S-F) = 89.9 \pm 3.4 \text{ kcal/mole} = 3.9 \pm 0.15 \text{ eV}. \qquad (3)$$

As a result, the electron affinity of the SF_5 radical is recalculated to be

$$\text{E. A. } (SF_5) \geq 3.4 \pm 0.2 \text{ eV}. \qquad (4)$$
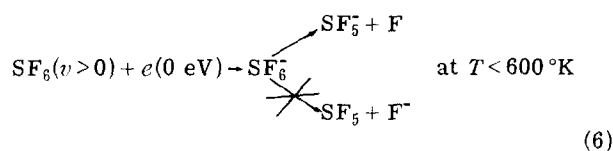
The same correction applies to data from experiments[5] on collisional ionization between fast alkali atoms and SF_6, leading to exactly the same result [Eq. (4)].

The new value of $D_0^o(F_5S-F)$ has no effect on the threshold energy for dissociative electron capture process,

$$e + SF_6 \rightarrow SF_5^- + F \qquad (5)$$

which remains at $D_0^o(F_5S-F) - \text{E. A. } (SF_5) = 0.5 \text{ eV}$ in agreement with experimental results.[1,6,7]

The SF_6^- negative molecule ion has been demonstrated[6,] to follow the quasiequilibrium theory (QET) of mass spectra. According to the QET, the two processes forming F^- and SF_5^- from SF_6^- are in competition and the process possessing the lower activation energy will take place preferentially at low energies. Lifshitz and Weiss[6] as well as Chen and Chantry[9] have not observed F^- by dissociative electron capture from SF_6 at zero electron energy and at temperatures below $600\,^\circ$K. They did observe SF_5^- under the same conditions, due to the reaction of vibrationally excited SF_6,

$$SF_6(v > 0) + e(0 \text{ eV}) \rightarrow SF_6^- \begin{array}{c} \nearrow SF_5^- + F \\ \\ \searrow\!\!\!\!\times\; SF_5 + F^- \end{array} \quad \text{at } T < 600\,^\circ\text{K} \qquad (6)$$

The electron affinity of the fluorine atom is very accurately known[10] to be E. A. $(F) = 3.399 \pm 0.003$ eV. The behavior in accordance with Eq. (6) supports the result that the electron affinity of SF_5 is greater than that of Fluorine.

[1]C. Lifshitz, T. O. Tiernan, and B. M. Hughes, J. Chem. Phys. **59**, 3182 (1973).
[2]T. L. Cottrell, *The Strength of Chemical Bonds* (Butterworths, London, 1958).
[3]D. L. Hildenbrand, J. Phys. Chem. **77**, 897 (1973).
[4]T. Kiang, R. C. Estler, and R. N. Zare, J. Chem. Phys. **70**, 5343 (1979).
[5]R. N. Compton, P. W. Reinhardt, and C. D. Cooper, J. Chem. Phys. **68**, 2023 (1978).
[6]C. Lifshitz and M. Weiss, Chem. Phys. Lett. **15**, 266 (1972).
[7]F. C. Fehsenfeld, J. Chem. Phys. **53**, 2000 (1970).
[8]C. Lifshitz, A. MacKenzie Peers, R. Grajower, and M. Weiss, J. Chem. Phys. **53**, 4605 (1970).
[9]C. L. Chen and P. J. Chantry, Bull Am. Phys. Soc. **15**, 418 (1970).
[10]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).