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Correlation formula for the couplings at crossings between ionic and covalent molecular states

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From an analysis of empirical and theoretical information on ionic and covalent interactions, a relationship is established between the coupling matrix elements (which measure the nonadiabatic splitting at avoided crossings and strongly influence transition probabilities) and basic quantities of separated partners (ionization potentials, electron affinities, polarizabilities). Although the systems considered here are limited to alkali atoms interacting with simple atoms and molecules, the proposed correlation rule paves the way for extensions to deal with electron transfer reaction dynamics for more general donor-acceptor couples. © 1997 American Institute of Physics. [S0021-9606(97)01610-3]

I. INTRODUCTION

The nature of many phenomena in molecular structure and reactivity can be described by a universal mechanism involving electron transfer between two systems. The simplest and more general examples are the formation of the bond in ionic molecules and the reactivity of metal atoms: the ionic bond in alkali halides (and also in some excimer molecules) is the result of the interaction of covalent and Coulomb forces; the 'harpoon' reaction mechanism¹ is triggered by the jump of the electron from the metal to molecules to form positive and negative ions, which then strongly attract each other and proceed to react.² Implications for modeling complex systems, up to those of biological interest, are ubiquitous and listed recently.³

For the modeling of elementary chemical processes we modernly need to know the involved interactions accurately, and this is becoming available now that open shell and anisotropy contributions to long range forces are measured and understood thanks to molecular beam scattering and to spectroscopy experiments. Actually, processes such as ion-recombination,⁴ energy transfer,⁵ ion-molecule reactions⁶ require characterization of the relevant interactions, including *coupling terms*. As far as dynamics is concerned, recent definitive progress has taken place on the treatment of these processes, well beyond the original Landau-Zener formula for curve crossing problems, for which both exact⁷ and powerful approximate solutions³ are now available. These formulations, as well as elaborate dynamical calculations,⁸ rely on the knowledge of the couplings: it is our aim to provide here a correlation rule for their estimation.

In the next section, a systematic procedure is presented for the characterization of ionic and covalent interactions, by specializing to systems involving alkali atoms and various atomic and molecular partners, the empirical recipes recently proposed in this laboratory⁹⁻¹¹ (see also the Appendix). Our correlation rule for the coupling terms, which extends previ-

ous proposal,^{12,13} is presented and tested in Sec. III. Some final remarks will follow in Sec. IV.

II. CHARACTERIZATION OF IONIC AND COVALENT INTERACTIONS

Figure 1 serves to introduce the relevant notations. In quantum mechanics, the interaction is written as a matrix (all entries depending on internuclear coordinates):

$$\begin{pmatrix} V_{\text{ion}} & V_{\text{ion,cov}} \\ V_{\text{ion,cov}} & V_{\text{cov}} \end{pmatrix}, \quad (1)$$

where V_{ion} and V_{cov} are diabatic states or *diabats* and $V_{\text{ion,cov}}$ is the coupling matrix element — the target of this paper. In general V_{ion} lies higher than V_{cov} at large distance, but the interaction being Coulombic ($\sim R^{-1}$), and stronger than the van der Waals interaction ($\sim R^{-6}$ at long range) operative in V_{cov} , the two come closer as the distance decreases: at the diabatic crossings the alternative description is in terms of adiabatic curves (*adiabats*, dashed in the inset of Fig. 1), the eigenvalues of (1).

The Landau-Zener formula, as well as recent improvements,³ associates slow motion as evolution on adiabats and fast motion to evolution on diabats: coupling matrix elements influence exponentially the transition probabilities between states and therefore are a crucial ingredient of dynamics calculations. They are however elusive, because they need to be extracted from analysis of perturbations in spectra or of difficult (although recently feasible) molecular beam scattering experiments: quantum chemistry is here having its greatest difficulties, because the calculation of these matrix elements, as overlap integrals between ionic and covalent wavefunctions, involves the basic problem of dealing properly with configuration interaction.¹⁵

In previous work, we have been trying to compact a wealth of information, made available in recent times through various sources, on intermolecular forces, in order to look at simple correlations with properties of the separate partners, with the aim of both understanding the nature of these forces and of anticipating their strength and range for unknown systems.⁹⁻¹¹

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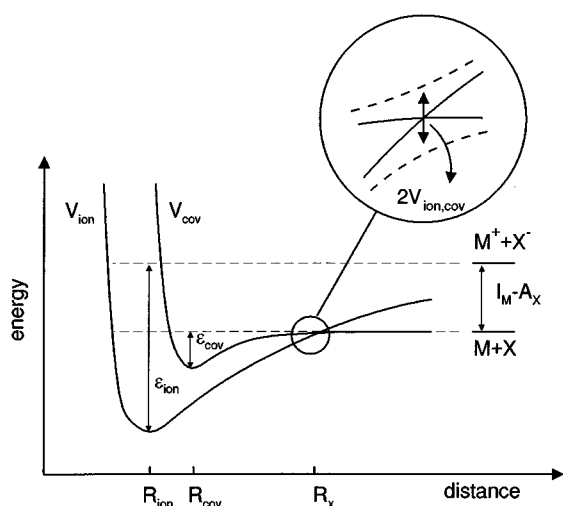


FIG. 1. Schematic representation of the ionic and covalent interactions V_{ion} and V_{cov} , between a donor M and an acceptor X ; these interactions are here pictured as depending on a distance parameter R and shown as undergoing a *diabatic* crossing at R_x , where they interact through a coupling matrix element $V_{\text{ion,cov}}$ [Eq. (1)]. Noncrossing adiabats are shown as dashed in the inset. In general all quantities V_{ion} , V_{cov} , and $V_{\text{ion,cov}}$ may depend on more variables than a single distance parameter, and molecular anisotropy and manifolds of surfaces arising from orbital and spin-orbit effects have to be included, Ref. 14. For the metal halides treated explicitly here, the latter effects split the covalent curve in eight states, only those of the same symmetry of the ionic curve ($^1\Sigma$) are actually interacting with it through $V_{\text{ion,cov}}$.

Now the ionic interactions are reasonably understood: our account on them from the viewpoint relevant for present work is available¹¹ and allows the proper account of the contribution of dispersion and induction forces to the Coulombic attraction. Covalent interactions are much weaker and less known:^{16,17} they will be briefly discussed here, especially because it will turn out that their strength ϵ_{cov} will be an essential ingredient to establish a correlation rule for $V_{\text{ion,cov}}$. Table I reports ϵ_{cov} and R_m^{cov} for systems of alkali atoms with halogens (both atoms and diatoms: for the latter R is measured from the alkali atom to the center of mass of the molecule), as estimated from our recipes⁹ (their meaning as proper average values over fine structure, orbital, and possibly orientational, anisotropy is discussed in Ref. 11). Relevant formulas are reported in the Appendix.

These systems are prototypical for discussion of ionic bonds and of metal reactions by the harpoon mechanism; a particular feature serves to simplify the following discussion, but is not an intrinsic limitation of the present approach.

The correlation formulas used for the entries in the table⁹ have among their ingredients the polarizabilities α_M and α_X : actually, for all present cases (and for nearly all the physically interesting ones) the inequality between polarizabilities $\alpha_M > \alpha_X$ holds. So, as a consequence, it is immediate to show that both ϵ_{cov} and R_m^{cov} depend chiefly on α_X and α_M , respectively; simplified formulas, in working units, are easily worked out as follows:

$$\bar{\epsilon}_{\text{cov}} = 0.44\alpha_X, \text{ meV}; \quad \bar{R}_m^{\text{cov}} = 2.49\alpha_M^{0.14} \text{ \AA}, \quad (2)$$

TABLE I. Energy and position of minima of covalent interactions.^a

R_m^{cov} (\AA)		F	Cl	Br	I	F ₂	Cl ₂	Br ₂	I ₂	\bar{R}_m^{cov}
ϵ_{cov} (meV)										
Li		5.13	5.08	5.10	5.17	5.08	5.15	5.22	5.32	5.08
		1.8	7.0	9.5	15.0	4.6	13.5	18.7	25.6	
Na		5.11	5.06	5.08	5.15	5.05	5.13	5.20	5.31	5.06
		2.1	8.2	11.2	17.5	5.5	15.9	21.8	29.7	
K		5.66	5.52	5.51	5.54	5.54	5.53	5.57	5.64	5.51
		1.6	7.1	9.9	16.4	4.5	14.6	21.0	30.0	
Rb		5.75	5.59	5.58	5.60	5.62	5.59	5.63	5.70	5.58
		1.6	7.0	9.8	16.3	4.4	14.5	21.0	30.2	
Cs		5.99	5.79	5.77	5.78	5.83	5.77	5.80	5.85	5.76
		1.4	6.4	9.1	15.6	4.0	13.8	20.2	29.6	
$\bar{\epsilon}_{\text{cov}}$		1.7	6.5	9.1	16.0	4.1	13.8	21.1	33.2	

^aEntries ϵ_{cov} and R_m^{cov} are calculated from formulas reported in the Appendix (see also Ref. 9), using polarizabilities from Ref. 18. Simplified values $\bar{\epsilon}_{\text{cov}}$ and \bar{R}_m^{cov} follow from Eq. (2).

where polarizabilities are in units of $a_0^3 = 0.1481845 \text{ \AA}^3$. The reliability of these estimates can be appreciated from the table.

III. THE COUPLING: A CORRELATION FORMULA

Olson, Smith, and Bauer,¹² reviewing previous work,^{19,20} give arguments for representing the dependence of coupling matrix elements $V_{\text{ion,cov}}$ from the crossing radius R_x as a decreasing exponential in reduced variables

$$V_{\text{ion,cov}}^* = \frac{V_{\text{ion,cov}}}{(I_M A_X)^{1/2}}; \quad R_x^* = R_x \left(\frac{I_M^{1/2} + A_X^{1/2}}{2^{1/2}} \right), \quad (3)$$

where I_M is the ionization potential of the donor metal atom and A_X the electron affinity of the acceptor (the vertical value in the case of molecules) and all the quantities are — here and in the following of this section — in atomic units (i.e., energies in units of $2I_H = 27.212 \text{ eV}$, and distances in units of $a_0 = 0.529177 \text{ \AA}$).

Although the original correlation formula was not too accurate, showing a large dispersion over the many systems considered, it was later shown by Grice and Herschbach¹³ that inclusion of more data and higher accuracy lead to the conclusion that the proposed scaling and correlations were valid only within given families (fluorides, chlorides, ...): for example, for the family of alkali iodides,

$$V_{\text{ion,cov}}^* = 2.44R_x^* \exp[-R_x^*]. \quad (4)$$

The formula well reproduces the R dependence for all systems, but the numerical coefficient has to be changed for different acceptor atoms or molecules. We need a better scaling for $V_{\text{ion,cov}}$ to compact all data.

To achieve this, we must consider recent available empirical information on configuration interaction as obtained from the analysis of experimentally derived charge transfer contributions to bonds of open shell atoms (oxygen, fluorine, chlorine) with closed shell systems²¹ (the rare gases, simple

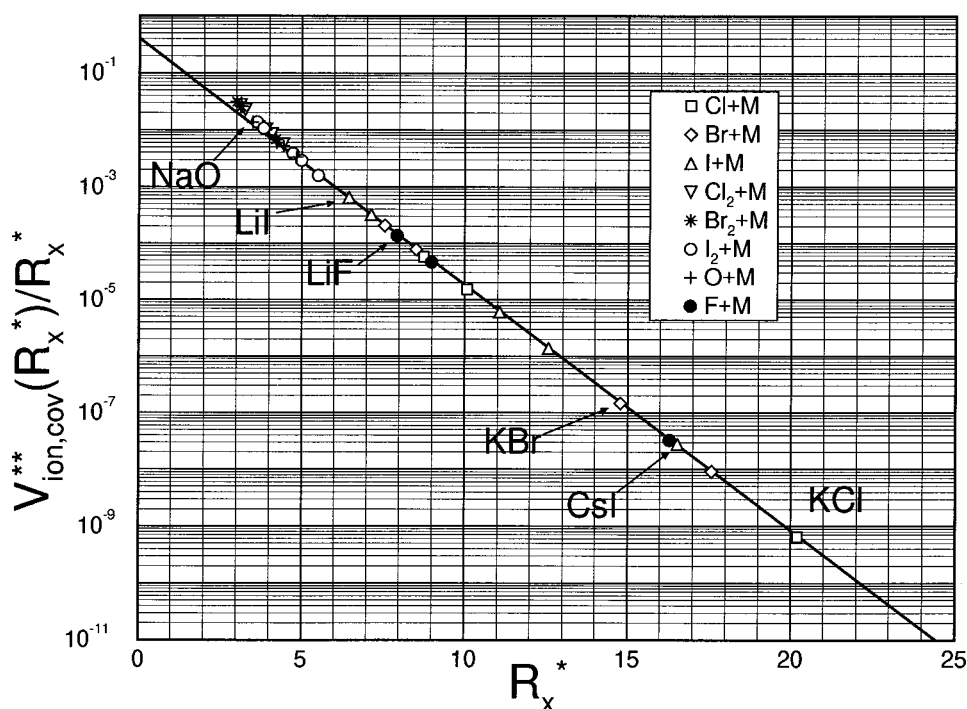


FIG. 2. Ratios of the reduced quantity $V_{\text{ion,cov}}^{**}(R_x^*)$ [Eq. (6)] and the reduced crossing distance R_x^* [Eq. (3)] reported versus R_x^* on a semilogarithmic plot. The straight line is Eq. (5). The data are all those in a similar plot in Ref. 13 except the hydride systems (see text).

molecules). For these systems, the ground (covalent) and the excimer (ionic) states, V_{cov} and V_{ion} in (1), do not cross but the $V_{\text{ion,cov}}$ term plays its role stabilizing the ground states and destabilizing the excimer states: it is empirically found for these cases²² that configuration interaction depends on the ratio between $V_{\text{ion,cov}}^2$ and the energy separation between V_{ion} and V_{cov} . Moreover in the region where $V_{\text{cov}} \sim 0$, a correlation has been derived and tested²² between (the square of) the coupling due to charge transfer and the strength of the covalent interaction. In such a region, where V_{cov} changes sign, *attraction* (due to induction and polarization forces, $V_{\text{attr}} \propto \epsilon_{\text{cov}}$) and *repulsion* (due to orbital overlap, $V_{\text{rep}} \propto V_{\text{ion,cov}}^2$) effectively balance, so that $V_{\text{ion,cov}}^2 \propto \epsilon_{\text{cov}}$, the link being provided by the fact that both depend on electron overlap: a universal proportionality law is proposed in Ref. 22.

Extending this argument, we suggest $V_{\text{ion,cov}}^{**}$ to be further reduced by $\epsilon_{\text{cov}}^{1/2}$ or more simply by $\alpha_X^{1/2}$ [see Eq. (2)] to give

$$V_{\text{ion,cov}}^{**} = 0.406 R^* \exp[-R^*], \quad (5)$$

where

$$V_{\text{ion,cov}}^{**} = \frac{V_{\text{ion,cov}}^{*}}{\alpha_X^{1/2}} = \frac{V_{\text{ion,cov}}}{(I_M A_X \alpha_X)^{1/2}}. \quad (6)$$

Systems under focus are for simplicity families of alkali atoms interacting with halogen and oxygen atoms and halogen molecules, already considered by Olson, Smith, and

Bauer¹² and then more extensively by Grice and Herschbach,¹³ whose data have been taken to produce the plot shown in Fig. 2.

The numerical factor in (5) was simply obtained by scaling the iodine family law (4) by $\alpha_I^{1/2}$,¹⁸ so the figure shows that no adjustment is needed to produce an impressively accurate fit of the other seven families: the best fit, indistinguishable in Fig. 2, leads to the numerical factor in (5) higher by $\sim 10\%$.

So far we have considered the simplest possible models, whose understanding is however basic for more general donor-acceptor cases. To keep the presentation sufficiently concise, we have only included the original data considered in Ref. 13 (excluding however the hydrides, see next section): however, we think that the correlation of Fig. 2, which spans several decades of coupling strengths over a wide range of crossing radii, appears to set the reference with respect to which further work has to be confronted — also possibly to discuss the underlying reasons in case of serious departures.

IV. REMARKS AND CONCLUSIONS

One important case is represented by the alkali hydrides, for which some of the assumptions on the asymptotic form of wavefunctions underlying this treatment has to be relaxed.²²

In particular the asymptotic wavefunction tails of the hydride ion and of the hydrogen atom cannot be assumed to be similar.²³ It is easy to show that accordingly our formula,

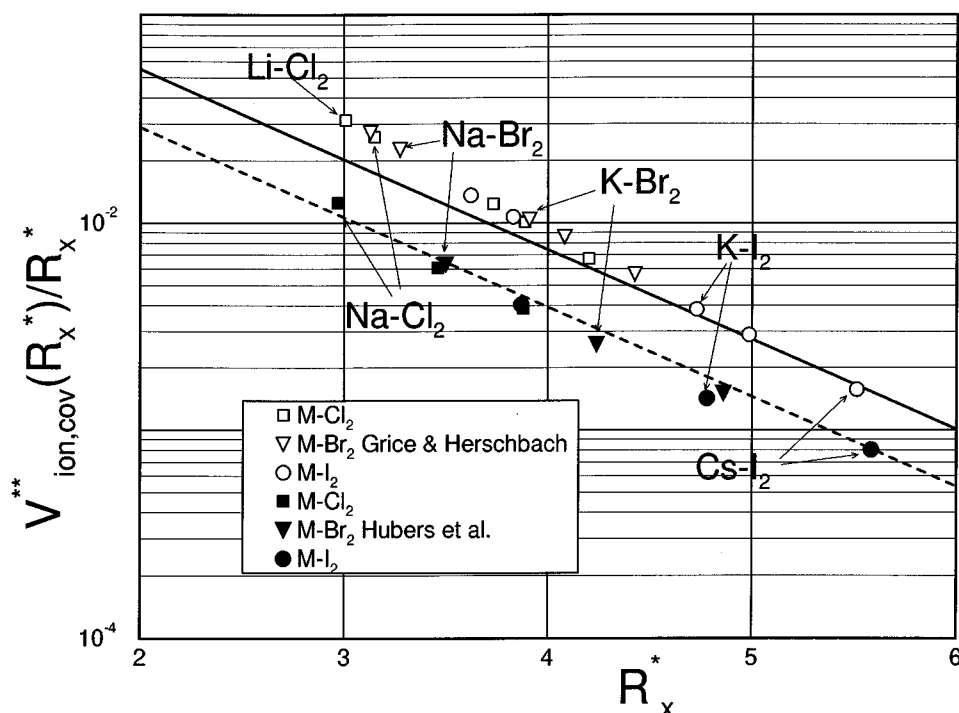


FIG. 3. Ratios of the reduced quantity $V_{\text{ion,cov}}^{**}(R_x^*)$ [Eq. (6)] and the reduced crossing distance R_x^* [Eq. (3)] reported versus R_x^* on a semilogarithmic plot for the case of alkali atom-halogen molecule systems. The straight line is Eq. (5). The dashed line is Eq. (5) with the numerical factor divided by 2. Open symbols are from Ref. 13, which include all five alkalis from Li to Cs, while full symbols are from Ref. 24, which only consider Na, K, and Cs.

Eq. (5), should underestimate the couplings of at least a factor of 2. Data on the couplings at crossings of ground electronic states of alkali hydrides from Grice and Herschbach,¹³ excluded from Fig. 2, exhibit a slope in agreement with Eq. (5) but the absolute values are higher by a factor of 3 with respect to Eq. (5). Other data on the alkali hydride from literature²³ also show a slope in accord with Eq. (5), while the absolute values range in between those of Grice and Herschbach and those predicted by Eq. (5). Therefore for these systems our correlation provides a lower limit for the coupling at the crossings, but should not be interpreted as discriminating any set of literature data with respect to the others.

Analogous considerations (similarity of slopes, underestimation of absolute values) also arise from the analysis of the characteristics of the ionic-covalent crossings involving the covalent curves correlating with the low lying excited states of alkali atoms.

As illustrated before our correlation (5) is based on atom-atom systems. What can we say about atom-molecule pairs? As we have seen, taking into account the data of Grice and Herschbach leads to the numerical factor in (5) higher by $\sim 10\%$ but some remarks are in order, in view also of newer data.

In general, there is an intrinsically larger uncertainty associated with the evaluation of the coupling at crossings for atom-molecule systems (see also Ref. 24 and Fig. 3). This mainly comes out from the not unique choice for the electron affinity (adiabatic versus vertical): recent advances in our understanding of the time involved in an electronically nona-

diabatic transition can help to elucidate this point.^{5,26} Also the angular dependence of the coupling matrix elements²⁵ introduce additional complexities not present in the case of atoms.

More details can be appreciated from Fig. 3. It should be noted how all the families analyzed both by Grice and Herschbach¹³ and Hubers *et al.*²⁴ normalize naturally once scaled as suggested in this paper: this is a further support of the proposed proportionality of the (square of the) coupling matrix element with the van der Waals strength parameter ϵ and thus with the acceptor polarizability. The proportionality factor is however about one-half lower for the data from Ref. 27.

This is perhaps not too surprising in view of experimental uncertainties. Both sets of data have been analyzed by the authors of Refs. 13 and 24 under the severe assumption of crossings determined solely by the Coulombic interaction: Table I clearly shows how most of the crossings actually occur at distances smaller than R_m^{cov} (the position of the minimum of the covalent curve), so presumably in the repulsive

TABLE II. Long range C_6 coefficients of covalent interactions in eV Å⁶.

	F	Cl	Br	I	F ₂	Cl ₂	Br ₂	I ₂
Li	45	167	233	398	110	350	525	811
Na	52	192	267	454	127	402	600	924
K	74	276	386	660	181	580	871	1350
Rb	79	295	411	704	193	619	929	1440
Cs	90	337	470	806	219	707	1060	1650

region of the latter. Furthermore it is clear that induction and dispersion contributions cannot be neglected in this intermolecular distance range.¹¹ All these factors should contribute to shift the crossings at larger distances with a consequent, but not easily estimable, change in the coupling values.

Kleyn *et al.*²⁷ also investigated the alkali-O₂ systems, for which however application of Eq. (5) is not guaranteed because of the negligible electron affinity of oxygen. For these and in general also for other more complicated cases²⁸ we also know how to proceed to improve upon some of the simplifications that we have introduced.²² And it is clear that we tend to attribute to the type of correlations found also a predictive power, that will allow us to anticipate in a reasonable way the couplings for a variety of acceptor-donor systems in terms of simple properties of the separated partners, such as ionization potentials, electron affinities, and polarizabilities.

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APPENDIX: EMPIRICAL FORMULAS FOR NEUTRAL-NEUTRAL INTERACTIONS

The following correlation formulas for the calculation of the parameters needed to model covalent interactions (i.e., R_m^{cov} , ϵ_{cov} , and C_6 , see also Fig. 1), as a function of the polarizabilities α_A and α_B of the interacting neutral partners A and B, have been developed and successfully tested recently:⁹

$$R_m^{\text{cov}} = 1.767 \cdot \frac{\alpha_A^{1/3} + \alpha_B^{1/3}}{(\alpha_A \alpha_B)^{0.095}} \text{ \AA}, \quad (\text{A1})$$

$$C_6 = 15.7 \cdot \frac{\alpha_A \alpha_B}{(\alpha_A/N_A)^{1/2} + (\alpha_B/N_B)^{1/2}} \text{ eV \AA}^6, \quad (\text{A2})$$

$$\epsilon_{\text{cov}} = 0.720 \cdot \frac{C_6}{R_m^6} \text{ meV}, \quad (\text{A3})$$

where polarizabilities are in \AA^3 (those needed here are taken from Ref. 18).

For the effective number of electrons N , to be used in Eq. (A2), following the guidelines reported in Ref. 9, we obtain $N=1.22, 1.74, 1.85, 1.92$, and 1.95 for Li, Na, K, Rb, Cs, $N=6.14, 7.73, 10.36$, and 11.47 for F, Cl, Br, I, and $N=14.2, 16.7$, and 19.5 for the molecules Cl₂, Br₂, I₂, respectively.

Equations (A1) and (A3) provide entries for Table I. Although not explicitly needed in this work, C_6 values from Eq. (A2) may have an intrinsic interest and therefore are listed in Table II. Formulas (A1)–(A3), originally derived

and tested for van der Waals interactions between closed shell neutrals, are here used to model the *isotropic*^{9,14} component of V_{cov} , i.e., averaged over orientation of *molecules* or fine structure and orbital alignment of *open shell atoms*.

Further material along these lines for interactions involving ions can be found in Refs. 10 and 11.

- ¹M. Polanyi, *Atomic Reactions* (Williams and Norgate, London, 1932); J. L. Magee, *J. Chem. Phys.* **8**, 687 (1940); D. R. Herschbach, *Adv. Chem. Phys.* **10**, 319 (1966).
- ²See the reviews, R. K. Janev, *Adv. At. Mol. Phys.* **12**, 1 (1976); A. W. Kleyn, J. Los, and E. A. Gislason, *Phys. Rep.* **90**, 1 (1982); M. I. Chibisov and R. K. Janev, *ibid.* **166**, 1 (1988); P. R. Brooks, *Int. Rev. Phys. Chem.* **14**, 327 (1995).
- ³H. Nakamura and C. Zhu, *Comments At. Mol. Phys.* **32**, 249 (1996), and references therein.
- ⁴V. Aquilanti, R. Candori, S. V. K. Kumar, and F. Pirani, *Chem. Phys. Lett.* **237**, 456 (1995), and references therein.
- ⁵V. Aquilanti, R. Candori, F. Pirani, T. Krümpelmann, and Ch. Ottinger, *Chem. Phys.* **142**, 47 (1990); V. Aquilanti, R. Candori, F. Pirani, and Ch. Ottinger *ibid.* **187**, 171 (1994), and references therein.
- ⁶P. Tosi, F. Eccher, D. Bassi, F. Pirani, D. Cappelletti, and V. Aquilanti, *Phys. Rev. Lett.* **67**, 1254 (1991); P. Tosi, O. Dmitrijev, Y. Soldo, D. Bassi, D. Cappelletti, F. Pirani, and V. Aquilanti, *J. Chem. Phys.* **99**, 985 (1993), and references therein.
- ⁷C. Zhu, H. Nakamura, N. Re, and V. Aquilanti, *J. Chem. Phys.* **97**, 1892 (1992).
- ⁸Femtosecond experiments are also being pioneered in this context, see M. J. Rosker, T. S. Rose, and A. H. Zewail, *Chem. Phys. Lett.* **146**, 175 (1988); P. Cong, G. Roberts, J. L. Herek, A. Mohktai, and A. H. Zewail, *J. Phys. Chem.* **100**, 7832 (1996), and the corresponding theoretical papers V. Engel and H. Metiu, *J. Chem. Phys.* **90**, 6116 (1989) and T. J. Martinez and R. D. Levine, *Chem. Phys. Lett.* **259**, 252 (1996).
- ⁹R. Cambi, D. Cappelletti, G. Liuti, and F. Pirani, *J. Chem. Phys.* **95**, 1852 (1991).
- ¹⁰D. Cappelletti, G. Liuti, and F. Pirani, *Chem. Phys. Lett.* **183**, 297 (1991).
- ¹¹V. Aquilanti, D. Cappelletti, and F. Pirani, *Chem. Phys.* **209**, 299 (1996).
- ¹²R. E. Olson, F. T. Smith, and E. Bauer, *Appl. Opt.* **10**, 1848 (1971).
- ¹³R. Grice and D. R. Herschbach, *Mol. Phys.* **27**, 159 (1974).
- ¹⁴V. Aquilanti, F. Pirani, G. Liuti, and F. Vecchiocattivi, *J. Chem. Soc. Faraday Trans. 2* **85**, 955 (1989).
- ¹⁵See, M. D. Newton, *Chem. Rev.* **91**, 767 (1991) and references therein, also for implications for more complex systems than those considered here, and for the role of nonadiabatic effects on Marcus adiabatic model for electron transfer in solution, R. A. Marcus, *Rev. Mod. Phys.* **65**, 599 (1993).
- ¹⁶R. S. Berry and W. Klemperer, *J. Chem. Phys.* **26**, 724 (1957); R. S. Berry, *ibid.* **27**, 1288 (1957); A. S. Ragone, D. H. Levy, and R. S. Berry, *ibid.* **77**, 3784 (1982).
- ¹⁷S. H. Schaefer, D. Bender, and E. Tiemann, *Chem. Phys. Lett.* **92**, 273 (1982); *ibid.* **89**, 65 (1984); *ibid.* **102**, 165 (1986); H. Bluhm, J. Lindner, and E. Tiemann, *J. Chem. Phys.* **93**, 4556 (1990).
- ¹⁸*CRC Handbook of Chemistry and Physics* (Chemical Rubber, Boca Raton, 1986), Vol. 67.
- ¹⁹D. Rapp and W. E. Francis, *J. Chem. Phys.* **37**, 2631 (1962).
- ²⁰B. M. Smirnov, *Sov. Phys. Dokl.* **10**, 218 (1965); *ibid.* **12**, 242 (1967). For recent related work, see E. E. Nikitin and B. M. Smirnov, *Slow Atomic Collisions* (Energoatomizdat, Moscow, 1990), and references therein.
- ²¹For the interaction of O(³P) atoms with simple atoms and molecules, see V. Aquilanti, E. Luzzatti, F. Pirani, and G. G. Volpi, *J. Chem. Phys.* **73**, 1181 (1980); V. Aquilanti, R. Candori, and F. Pirani, *ibid.* **89**, 6157 (1988); V. Aquilanti, R. Candori, L. Mariani, F. Pirani, and G. Liuti, *J. Phys. Chem.* **93**, 130 (1989). For F(²P) interactions, see V. Aquilanti, E. Luzzatti, F. Pirani, and G. G. Volpi, *Chem. Phys. Lett.* **90**, 382 (1982); *J. Chem. Phys.* **89**, 6165 (1988); V. Aquilanti, R. Candori, D. Cappelletti, E. Luzzatti, and F. Pirani, *Chem. Phys.* **145**, 293 (1990). For Cl(²P) interactions, see V. Aquilanti, D. Cappelletti, V. Lorent, E. Luzzatti, and F. Pirani, *Chem. Phys. Lett.* **192**, 153 (1992); *J. Phys. Chem.* **97**, 2063 (1993); V. Aquilanti, D. Cappelletti, and F. Pirani, *J. Chem. Soc. Faraday Trans.* **89**, 1467 (1993).
- ²²V. Aquilanti, D. Cappelletti, and F. Pirani, *Chem. Phys. Lett.* (in press).

The success of the proposed correlation relies on the simplification that for oxygen and the halogens (and in general for systems showing high electron affinities) the negative ion has an outer electronic distribution similar to that of the neutral (see Ref. 13).

- ²³D. R. Bates and T. J. M. Boyd, *Proc. Phys. Soc. A* **69**, 910 (1956); R. W. Numrich and D. G. Truhlar, *J. Phys. Chem.* **79**, 2745 (1975); R. K. Janev, *J. Chem. Phys.* **64**, 1891 (1976); S. A. Adelman and D. R. Herschbach, *Mol. Phys.* **33**, 793 (1977); R. W. Numrich, and D. G. Truhlar, *J. Phys. Chem.* **82**, 168 (1978).
- ²⁴M. M. Hubers, A. W. Kleyn, and J. Los, *Chem. Phys.* **17**, 303 (1976).
- ²⁵E. A. Gislason and J. G. Sachs, *J. Chem. Phys.* **62**, 2678 (1975).
- ²⁶S. V. Bobashev and V. A. Kharchenko, in *Electronic and Atomic Collisions*, book of abstracts XVII ICPEAC, edited by I. E. McCarthy, W. R. McGillivray, and M. C. Standage (Griffith University, Brisbane, Australia, 1991), p. 664.
- ²⁷A. W. Kleyn, M. M. Hubers, and J. Los, *Chem. Phys.* **34**, 55 (1978).
- ²⁸See, for example, R. F. M. Lobo, A. M. C. Moutinho, K. Lacmann, and J. Los, *J. Chem. Phys.* **95**, 166 (1991) for the K-nitromethane system and R. F. M. Lobo, A. M. C. Moutinho, and J. Los, *Chem. Phys.* **179**, 179 (1994) for the K-halobenzene system.