Franck-Condon Factors for the Ionization of H₂, HD, and D₂

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Franck-Condon factors for the following ionization transitions were computed assuming a Morse potential:

$$H_2\ X^1\Sigma_g^+\ (v=0) \rightarrow H_2^+\ X^2\Sigma_g^+(v=0 \rightarrow 15)$$

$$HD\ X^1\Sigma_g^+\ (v=0) \rightarrow HD^+\ X^2\Sigma_g^+(v=0 \rightarrow 15)$$

$$D_2\ X^1\Sigma_g^+\ (v=0) \rightarrow D_2^+\ X^2\Sigma_g^+(v=0 \rightarrow 15).$$
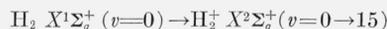
The results are used to interpret several recent ionization experiments which used essentially a monoenergetic ionizing medium. The relative importance of autoionization and direct ionization excitation processes are discussed.

1. Introduction

Recently, the use of monoenergetic electrons and photons in the investigation of the ionization of molecules has provided a large amount of information previously obscured by the energy spread of the ionizing medium. This information is contained in the structure of the ionization efficiency curves, i.e., the experimental curves relating the ion current per ionizing particle to the energy of the ionizing particle. In general the gross features of these ionization efficiency curves are related to the electronic transitions involved in the ionization process, while the fine structure observed in these curves is due to transitions involving vibrational excitation within the electronic states and autoionization transitions. Discussion of these finer details of electron or photon ionization of molecules necessitates having the Franck-Condon probabilities for transitions between vibronic states. In the Born-Oppenheimer approximation the probability of a transition is given by

$$P_{ev,e'v'} \sim | \int G_{e,e'}(R,r)\psi_{e,v}(R)\psi_{e',v'}(R)d\tau_R|^2,$$

where $\psi_{e,v}(R)$ and $\psi_{e',v'}(R)$ are the vibrational wave functions for the neutral molecule and ion, respectively [1].[1] If the variation of the perturbation integral $G_{e,e'}$ with R is small, then we have

$$P_{ev,e'v'} \sim |G_{e,e'}(R_e r)|^2 \cdot | \int \psi_{e,v}(R)\psi_{e',v'}(R)d\tau_R|^2.$$

Those features of the ionization efficiency curves that are due to transitions to the vibrational levels of the various electronic states of the ion can be described

to a good approximation by the vibrational overlap integral with the assumption of appropriate threshold behavior for the ionization process under investigation. For electron impact ionization near threshold $|G_{e,e'}|^2$ varies linearly with the excess energy above threshold [2]. For photoionization it is assumed that the probability near threshold can be approximated by a step function.

2. Method

The problems involved in the computation of these integrals have been discussed by Nicholls and co-workers [3]. Under Nicholls' direction a program was prepared at NBS for the 704 electronic digital computer (later modified for the 7094 computer) which will evaluate these integrals for a Morse oscillator. In this method Morse potentials are assumed, each member of the two families of wave functions $\psi_i(i=0 \rightarrow v_{max})$, $\psi_j(i=0 \rightarrow v_{max})$ is computed at 0.01-Å intervals and overlap integrals between all pairs are computed and squared [4]. The computer input data are ω_e, $\omega_e x_e$, r_e, μ_a, and v_{max} for the ground electronic state of the molecule and for each of the electronic states of the ion for which the vibrational transition probabilities are being computed.

3. Results

The Franck-Condon probabilities for the transitions,

$$H_2\ X^1\Sigma_g^+(v=0) \rightarrow H_2^+\ X^2\Sigma_g^+(v=0 \rightarrow 15),$$

$$HD\ X^1\Sigma_g^+(v=0) \rightarrow HD^+\ X^2\Sigma_g^+(v=0 \rightarrow 15),$$

and

$$D_2\ X^1\Sigma_g^+(v=0) \rightarrow D_2^+\ X^2\Sigma_g^+(v=0 \rightarrow 15)$$

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[1] Figures in brackets indicate the literature references at the end of this paper.

were computed using the data of table 1. Tables 2, 3, and 4 present all the vibrational transition probabilities that were computed for these ionization processes. More than 99 percent of the total probability was accounted for in each case.

TABLE 1. *Basic data**

State	ω_e	$\omega_e x_e$	r_e	μ_a	v_{max}
	cm^{-1}	cm^{-1}	Å		
HH $X^1\Sigma_g^+$	4395.2_4	117.90_5	0.7416_6	0.504066	0
HH+$X^2\Sigma_g^+$	2297	62.	1.060	.503928	15
HD $X^1\Sigma_g^+$	3817.09	94.958	0.7413_6	.671917	0
HD+$X^2\Sigma_g^+$	1989.5	46.5	1.06	.671762	15
DD $X^1\Sigma_g^+$	3118.4_6	64.09_7	0.7416_4	1.007363	0
DD+$X^2\Sigma_g^+$	1624.8	31.0	1.06	1.007217	15

*The data for the H$_2$, HD, and D$_2$ molecules and the H$_2^+$ ion were obtained from G. Herzberg, The Spectra of Diatomic Molecules (D. Van Nostrand Co., Inc., New York, N.Y. (1950)). The data for the other ionic species were calculated from physical constants and the data of the H$_2^+$ ion.

TABLE 2. *Franck-Condon probabilities* (P) *for the transitions* $H_2X^1\Sigma_g^+$, v''=0→$H_2^+ X^2\Sigma_g^+$, v'=0→15.

v'	E	ΔE	P	ΣP
	eV	eV		
0	0.1405	0.1405	0.0922	0.0922
1	.4099	.2694	.1751	.2673
2	.6639	.2540	.1959	.4632
3	.9026	.2387	.1700	.6332
4	1.1258	.2232	.1275	.7607
5	1.3337	.2079	.0874	.8481
6	1.5263	.1926	.0566	.9047
7	1.7034	.1771	.0355	.9402
8	1.8652	.1618	.0219	.9621
9	2.0116	.1464	.0134	.9755
10	2.1427	.1311	.0082	.9837
11	2.2584	.1157	.0051	.9888
12	2.3586	.1002	.0032	.9920
13	2.4436	.0850	.0020	.9940
14	2.5131	.0695	.0013	.9953
15	2.5673	.0542	.0008	.9961

½ $h\nu_0$(H$_2$) =2168.1 cm^{-1}=0.2688 eV.

TABLE 3. *Franck-Condon probabilities* (P) *for the transitions* HD $X^1\Sigma_g^+$, v''=0→HD+ $X^2\Sigma_g^+$, v'=0→15

v'	E	ΔE	P	ΣP
	eV	eV		
0	0.1219	0.1219	0.0647	0.0647
1	.3569	.2350	.1416	.2063
2	.5804	.2235	.1788	.3851
3	.7924	.2120	.1721	.5572
4	.9929	.2005	.1408	.6980
5	1.1818	.1889	.1037	.8017
6	1.3593	.1775	.0712	.8729
7	1.5251	.1658	.0467	.9196
8	1.6795	.1544	.0298	.9494
9	1.8223	.1428	.0186	.9680
10	1.9536	.1313	.0116	.9796
11	2.0734	.1198	.0072	.9868
12	2.1816	.1082	.0044	.9912
13	2.2783	.0967	.0028	.9940
14	2.3635	.0852	.0018	.9958
15	2.4371	.0736	.0011	.9969

½ $h\nu_0$ (HD) =1884.8 cm^{-1}=0.2337 eV.

TABLE 4. *Franck-Condon probabilities* (P) *for the transitions* $D_2X^1\Sigma_g^+$, v''=0→$D_2^+ X^2\Sigma_g^+$, v'=0→15

v'	E	ΔE	P	ΣP
	eV	eV		
0	0.0998	0.0998	0.0354	0.0354
1	.2935	.1937	.0950	.1304
2	.4796	.1861	.1434	.2738
3	.6580	.1784	.1611	.4349
4	.8286	.1706	.1507	.5856
5	.9916	.1630	.1245	.7101
6	1.1470	.1554	.0943	.8044
7	1.2946	.1476	.0671	.8715
8	1.4345	.1399	.0456	.9171
9	1.5668	.1323	.0300	.9471
10	1.6914	.1246	.0193	.9664
11	1.8083	.1169	.0122	.9786
12	1.9174	.1091	.0077	.9863
13	2.0190	.1016	.0048	.9911
14	2.1128	.0938	.0030	.9941
15	2.1989	.0861	.0019	.9960

½ $h\nu_0$ (D$_2$) =1543.2 cm^{-1}=0.1913 eV.

4. Discussion

The computed values of the vibrational transition probabilities permit a closer look at several ionization experiments. Kerwin and coworkers [5] have examined the ionization efficiency curve of H$_2$ using a monoenergetic electron beam with an energy spread of about 0.03 eV. This permitted the observation of the vibrational states excited in the electron-impact ionization process. The observed vibrational transition probabilities up to the fourth vibrational level of the H$_2^+$ $X^2\Sigma_g^+$ ion are compared in table 5 with the theoretical values of this work and of Krauss and Kropf [6]. They calculated the Franck-Condon factors for the transitions H$_2$ $X^1\Sigma_g^+$, $v=0$→H$_2^+ X$ $^2\Sigma_g^+$, $v=0$→5 and D$_2$ $X^1\Sigma_g^+$, $v=0$→D$_2^+$ $X^2\Sigma_g^+$, $v=0$→5, using the data of Richardson [7]. The experimental electron-impact values for the vibrational transition probabilities (obtained with mass analysis of the ionization products) and the previously calculated values compare well with the computed values of this work. Vibrational levels in the electron-impact ionization efficiency curve for H$_2$ were also found by Weingartshofer and Clarke [8]. These appear to follow the predicted trend (table 2) in the relative transition probabilities to the vibrational levels in the H$_2^+$ ion.

TABLE 5. *Comparison of experimental electron-impact vibrational transition probabilities for* H$_2$ *with the theoretical Franck-Condon factors*

	Vibrational excitation transition, H$_2$(X)→H$_2^+$(X)				
	0–0	0–1	0–2	0–3	0–4
Experimental [5]	0.53	0.91	1.00	0.35	0.35
Theoretical:					
(a)	0.47	0.89	1.00	0.87	0.65
(b)	0.44	0.87	1.00	0.91	0.72

a This work.
b Krauss, ref. [6], using the vibrational constants of Richardson, ref. [7].

Dibeler and Reese [9] reported the ionization efficiency curves for H_2, HD, and D_2, obtained by photoionization followed by mass analysis. The energy spread in their photon beam is 2Å (about 0.03 eV). They observed a difference for the ionization energies of D_2 and H_2 of 0.04 eV, the value calculated from the data of tables 2 and 4 is 0.0367 eV.

Autoionization phenomena are prevalent in the photoionization efficiency curves for hydrogen and almost completely obscure the vibrational transitions. Autoionization, in general, appears as more or less broadened and asymmetric peaked functions depending upon the lifetimes of the states involved. The resultant photoionization efficiency curve for a molecule in which both autoionization transitions and direct ionization are probable would be composed of a series of steps due to the Franck-Condon vibrational level interaction with peaks due to the autoionization transitions superimposed upon the steps. Krauss [10] discusses the origin of the autoionization peaks and the relative probabilities for the direct ionization and autoionization processes in hydrogen. The autoionization arises from excitation to at least the D, D′, and B″ [11] electronic states of the H_2 molecule.

5. Conclusion

More detailed knowledge of the autoionization transitions and the predissociation of the electronic states of the molecules and ions is needed to completely determine theoretically the origin of the observed structure in ionization efficiency curves. Since total electronic transition probabilities based upon theoretical considerations are lacking, the complete a priori synthesis of these curves for hydrogen from the computed values of the Franck-Condon factors is not possible. Any complete theoretical discussion and synthesis of the ionization efficiency curves for hydrogen will require not only the prediction of the relative importance of autoionization processes as compared to direct ionization excitation but will also have to account for the dependence of the total electronic transition probabilities upon the medium of excitation.

6. References

[1] A. S. Coolidge, H. M. James, and R. D. Present, J. Chem. Phys. **4,** 193 (1936).
[2] D. R. Bates, A. Fundaminsky, J. W. Leech, and H. S. W. Massey, Trans. Roy. Soc. (London) **A243**, 93 (1950); S. Geltman, Phys. Rev. **102,** 171 (1956); R. E. Fox, W. M. Hickman, and T. Kjeldaas, Phys. Rev. **89,** 355 (1953); G. H. Wannier, Phys. Rev. **100,** 1180 (1956).
[3] W. R. Jarmain and R. W. Nicholls, Can. J. Phys. **32,** 201 (1954).
[4] R. W. Nicholls, J. Res. NBS **66A,** 227 (1962).
[5] L. Kerwin, P. Marmet, and E. M. Clarke in Advances in Mass Spectrometry, II, ed. R. M. Elliott (Pergamon Press, London, 1963), pp. 522–526.
[6] M. Krauss and A. Kropf, J. Chem. Phys. **26,** 1776 (1957).
[7] O. W. Richardson, Nuovo cimento **15,** 232 (1938).
[8] A. Weingartshofer and E. M. Clarke, Phys. Rev. Letters **12,** 591 (1964).
[9] V. H. Dibeler and R. M. Reese, Twelfth Annual Conference on Mass Spectrometry and Allied Topics, Montreal, Can. (June 1964) paper No. 44.
[10] V. H. Dibeler, R. M. Reese, and M. Krauss, Proc. 3d Intern. Conf. Mass Spectrometry, Paris, France (1964), to be published.
[11] A. Monfils, Bull. Classe Sci., Acad. roy. Belg. **47,** 816, (1961).

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