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LETTER TO THE EDITOR

Fully vibrationally resolved photoionisation of H_2 and D_2

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Abstract. Cross sections are computed for the photoionisation of H_2 and D_2 molecules in several vibrational states by 584 Å radiation, producing ions in a range of vibrational states. Both total cross sections (σ) and asymmetry parameters (β) are determined using the R-matrix method. Good agreement is obtained with recent experiments for the fully vibrationally resolved total cross sections of D_2. The β parameters decrease with vibrational excitation of the targets but also show structure which appears to be associated with Franck–Condon factors.

Photoionisation of molecular hydrogen is of great fundamental interest and has thus stimulated many studies, both theoretical and experimental. The vibrationally resolved photoionisation of ground state H_2 has been the subject of much work (see Itikawa 1987), which has led to a good understanding of this process. In particular, results are available, both rotationally and vibrationally resolved, for light of wavelength 584 Å (Hara and Ogata 1985, Chandra 1986, Hara and Nakamura 1986).

Little attention however appears to have been given to the possibility that the target molecule might be in a vibrationally excited state. Exceptions to this are calculations on H_2^* by O'Neill and Reinhardt (1978) and Tai and Flannery (1977), and the recent experimental results of Van der Meer *et al* (1985). None of these works determined the photoionisation asymmetry parameter β. There appears to be no knowledge of how β varies with vibrational excitation of the target. It would thus seem appropriate to extend one of the methods (Tennyson *et al* 1986) which has given reliable results on the photoionisation of ground-state H_2 to excited target states.

In this letter results for both total cross sections and asymmetry parameters are presented for the process

$$H_2(X^1\Sigma_g^+;\, v'') + h\nu \rightarrow H_2^+(X^2\Sigma_g^+;\, v') + e^- \qquad (1)$$

with $0 \leqslant v'' \leqslant 2$, and for the equivalent process for a D_2 target with $0 \leqslant v'' \leqslant 3$. The calculations closely follow those of Tennyson *et al* (1986) who performed photoionisation calculations using the polarised, two-state, R-matrix e^-–H_2^+ calculations of Tennyson *et al* (1984) and Tennyson and Noble (1985). The calculations included the lowest three partial waves for each of the H_2^+ target states. To accommodate vibrationally excited targets the calculations were performed using an extended grid of 13 fixed-nuclei calculations with the H_2 bond length ranging from 1.1 to 2.4 a_0. Vibrational wavefunctions for the target and ion were obtained by numerical solution (Le Roy 1971) of the Schrödinger equation for accurate H_2 (Bishop and Shih 1976) and H_2^+ (Bates *et al*

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1953) potentials. These were then used to obtain adiabatic photoionisation cross section parameters for a range of photon wavelengths.

Tables 1-4 present results for photons of wavelength 584 Å. Table 1 compares our total cross sections for H_2 with those of O'Neill and Reinhardt (1978). A more extensive comparison with the σ and β parameters for $v''=0$ can be found in Tennyson *et al* (1986). The agreement between the cross sections in table 1 is good, although our cross sections are consistently slightly larger. Analysis by O'Neill and Reinhardt shows that the structure displayed by these cross sections closely follows the Franck-Condon factors $|\langle v'|v''\rangle|^2$ and is thus not associated with the Feshbach resonances converging to the $^1\Sigma_u^+$ state of H_2^+ (Raseev 1985).

Table 1. Photoionisation cross sections in Mb for $H_2(v'') \rightarrow H_2^+(v')$ at 584 Å.

	$v''=0$		$v''=1$		$v''=2$	
v'	a	b	a	b	a	b
0	0.492	0.453	1.304	1.181	1.347	1.187
1	0.936	0.863	0.916	0.808	0.038	0.088
2	1.077	1.004	0.226	0.197	0.332	0.287
3	0.996	0.931	0.001	0.000	0.592	0.503
4	0.813	0.766	0.089	0.091	0.386	0.340
5	0.618	0.587	0.243	0.244	0.133	0.117
6	0.451	0.432	0.350	0.348	0.015	0.010
7	0.320	0.311	0.385	0.385	0.006	0.010
8	0.224	0.221	0.372	0.372	0.045	0.061

[a] This work.
[b] O'Neill and Reinhardt (1978).

Table 2. Photoionisation cross sections in Mb for $D_2(v'') \rightarrow D_2^+(v')$ at 584 Å.

	$v''=0$		$v''=1$		$v''=2$		$v''=3$	
v'	a	b	a	b	a	b	a	b
0	0.188	0.175	0.737	0.670	1.209	1.087	1.117	0.977
1	0.495	0.460	0.996	0.897	0.461	0.399	0.029	0.000
2	0.755	0.667	0.655	0.585	0.001	0.000	0.475	0.417
3	0.875	0.809	0.233	0.202	0.216	0.200	0.420	0.364
4	0.868	0.799	0.020	0.015	0.435	0.398	0.072	0.063
5	0.774	0.713	0.022	0.024	0.409	0.366	0.017	0.016
6	0.647	0.594	0.128	0.128	0.241	0.209	0.161	0.152
7	0.513	0.472	0.246	0.240	0.085	0.069	0.279	0.257
8	0.394	0.364	0.330	0.312	0.008	0.004	0.286	0.255
9	0.297	0.274	0.366	0.339	0.007	0.010	0.217	0.182
10	0.220	0.204	0.362	0.348	0.048	0.053	0.124	0.095
11	0.161	0.151	0.335	0.322	0.099	0.105	0.049	0.032

[a] This work.
[b] Van der Meer *et al* (1985).

Table 3. Photoionisation asymmetry parameters for $H_2(v'') \rightarrow H_2^+(v')$ at 584 Å.

	v''		
v'	0	1	2
0	1.806	1.735	1.591
1	1.832	1.768	1.661
2	1.859	1.800	1.745
3	1.880	1.282	1.762
4	1.897	1.833	1.793
5	1.911	1.866	1.825
6	1.922	1.884	1.890
7	1.932	1.898	1.646
8	1.940	1.909	1.840

Table 4. Photoionisation asymmetry parameters for $D_2(v'') \rightarrow D_2^+(v')$ at 584 Å.

	v''			
v'	0	1	2	3
0	1.810	1.761	1.702	1.602
1	1.832	1.787	1.721	0.966
2	1.851	1.810	0.901	1.709
3	1.867	1.830	1.785	1.719
4	1.881	1.851	1.809	1.725
5	1.894	1.847	1.824	1.741
6	1.905	1.872	1.852	1.804
7	1.914	1.885	1.868	1.824
8	1.922	1.897	1.877	1.868
9	1.930	1.906	1.832	1.868
10	1.936	1.914	1.876	1.876
11	1.941	1.921	1.892	1.888

Table 2 compares our total cross sections for D_2 with those derived by Van der Meer *et al* (1985). The agreement is good with our cross sections reproducing all the observed structure. Again our cross sections appear slightly larger.

Tables 3 and 4 present our predicted asymmetry parameters for H_2 and D_2 respectively. For both molecules the β parameters show an increase with increasing vibrational excitation of the ion and a decrease with vibrational excitation of the target. This latter trend is in agreement with Van der Meer *et al*'s interpretation of their observations. However, these changes are by no means monotonic. For several (v', v'') combinations anomalously small values of β are predicted. These all correspond to cases where the total cross section is greatly reduced by near-zero Franck-Condon factors. For example, the smallest calculated cross section is for photoionisation of D_2 in its $v''=2$ state producing D_2^+ with $v'=2$. This process also has the smallest predicted β parameter, being only just over half that which might have been expected by comparison with β values for nearby transitions.

In conclusion, calculated values are given for the fully vibrationally resolved photoionisation parameters for H_2 and D_2. Although these parameters display systematic trends with increasing vibrational excitation of the target, these trends must be considered with care due to occurrence of anomalously small values of the σ and β parameters. These anomalies appear to be associated with the near cancellation of the Franck-Condon overlaps of the target and ion vibrational wavefunction. The predicted structure in the β parameters is a new phenomenon which is not observed in photoionisation from the H_2 or D_2 ground state because their vibrational wavefunctions are nodeless.

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