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Reply to a comment by Weston on "IR lines broadened by chemical exchange"

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It is certainly true that the *possibility* of exchange broadening in the infrared and Raman has been mentioned in the literature for quite some time. However, as far as experimental evidence was concerned, the situation was summed up in 1965 by Weston himself, stating "... it is my opinion that the systems so far examined are not sufficiently free of complications unrelated to exchange broadening to constitute convincing experimental evidence that the latter phenomenon is indeed responsible."[1] Nor do we consider that the three post 1965 reports Weston mentions or the important contribution of David[2] have substantially altered this situation.

In our work,[3] where we concentrated on a very simple system, we were able to observe the separate lines of a complexed and uncomplexed species to broaden and shift towards one another, as the temperature was raised, until they almost coalesced. In the absence of the complexing agent the width of the uncomplexed line

changed only little over the same temperature range. We think these observations constitute the first experimental evidence for exchange broadening in the infrared. However, perhaps we would have done better to mention the early literature and then refer to our work as the first concrete experimental evidence.

Despite some doubts we had at the time we submitted our communication,[3] we now agree that the NMR line shape expressions should apply to the IR, and Raman, exchange broadened spectra as well.

Exchange broadening in the IR and Raman promises access to a number of different categories of reactions in the 0.1–10 psec range via very simple experiments.

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ERRATA

Erratum and comment: Rate constant and transmission coefficient in the diffusion theory of reaction rates [J. Chem. Phys. 72, 6606 (1980)]

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Equations (3.6) and (3.13) are too large by a factor of 2. The correct expression is

$$k \approx \frac{1}{\pi} \left[V''(x_0) | V''(\hat{x})| \right]^{1/2} \exp\{-[V(\hat{x}) - V(x_0)]/\epsilon\} . \quad (1)$$

Equation (1) is twice the value that Kramers obtained. This difference is explained as follows. The rate constant k above is the rate at which particles reach the top of the barrier. To calculate the rate at which particles reach the product state, this rate should be mul-

tiplied by the transmission coefficient, which is asymptotically $\frac{1}{2}$ at the top of the barrier, so that Kramers' original formula is obtained. Alternately, the first boundary condition Eq. (3.4) could be changed to $\sigma(x_1) = 0$ and the first boundary condition for the expected time could be changed to $T(x_1) = 0$, where $x_1 \gg x_0$. If this is done, the asymptotic analysis of Eqs. (3.5) and (3.11) give Kramers' original result. We note that the agreement with transition state theory will be even worse, if these modifications are made.

Erratum: Perturbation theory for the free energy of hard quadrupolar diatomics [J. Chem. Phys. 70, 5751 (1979)]

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In Eq. (2.12), $-4g_{221}^{\mathrm{HHD}}(r)$ should be $+4g_{221}^{\mathrm{HHD}}(r)$. [In Eq. (23) of Ref.(10), the $U_Q^{\mathrm{PERT}}(r_{12})|_{221}$ should be of positive sign.] As emphasized in the text, the large differences between the results for the 500-particle Monte Carlo runs and the 256-particle runs demonstrate that the Monte Carlo data are insufficiently precise to yield reliable Δf_1 estimates, although the order of magnitude of the estimates establish that the Δf_1 contributions are small compared to the Δf^P contributions.

The y values for $L = 0.6$ shown in Tables III, V, and VI are displaced; they are entered correctly in the Table below. In Eq. (2.6), $1/4$ should be y, while Eq. (2.7) should be

$$\beta \Delta f_0^B = \frac{(2\gamma - 3) + 2(\gamma^2/9 - \gamma + 3)\, y - 3y^2}{2(1-y)^2}$$

$$- (1 - \gamma^2/9)\ln(1-y) + \ln y \,, \qquad (2.7)$$

necessitating a change in the entries for Eq. (2.7) in Table III. The corrected entries, along with Fig. 1 redrawn in accordance with the corrected Table V is available from each author. We are grateful to W. A. Steele for pointing out a sign error in Eq. (2.12).

This changes the $\beta \Delta f_1 Q^2$ entries of Table V, which should be as below:

Corrections to TABLE V

ρ^*	y	$\beta\Delta f_1 Q^2$		
		$L = 0.4$ (N_2)		
		$T = 20.7^b$ K	$T = 77.4$ K	$T = 126.1$ K
0.2		-0.0128	-0.0034	-0.0021
0.3		-0.0217	-0.0058	-0.0036
0.4		$+0.0576$	$+0.0154$	$+0.0095$
0.5^a		-0.0652	-0.0174	-0.0107
0.6		$+0.0920$	$+0.0246$	$+0.0151$
0.6^a		-0.0903	-0.0241	-0.0148
		$L = 0.6$ (Cl_2)		
		$T = 172$ K	$T = 238.6$ K	$T = 417$ K
0.2	0.1877	-0.0414	-0.0298	-0.0171
0.3	0.2815	-0.0409	-0.0295	-0.0169
0.4	0.3753	-0.0682	-0.0492	-0.0282
0.5	0.4692	-0.4006	-0.289	-0.165
0.6	0.5620	$\cdots$	$\cdots$	$\cdots$

[a]500 particles.
[b]Although $T = 20.7$ K is used as a reference T for the $L = 0.4$ fluid in Ref. 10 and elsewhere, it is actually far too low a temperature to be relevant to the fluid state. (In N_2, the triple point is at 63.1 and an orientational-ordering transition takes place at ~ 35 K.)