

Role of Vibrational Dynamics in Resonant Positron Annihilation on Molecules

A. C. L. Jones, J. R. Danielson, M. R. Natisin, and C. M. Surko*

Department of Physics, University of California, San Diego, La Jolla, California 92093, USA

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Vibrational Feshbach resonances are dominant features of positron annihilation for incident positron energies in the range of the molecular vibrations. Studies in relatively small molecules are described that elucidate the role of intramolecular vibrational energy redistribution into near-resonant multimode states, and the subsequent coupling of these modes to the positron continuum, in suppressing or enhancing these resonances. The implications for annihilation in other molecular species, and the necessary ingredients of a more complete theory of resonant positron annihilation, are discussed.

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Positron annihilation is important in a variety of contexts including astrophysics, materials science, and medical imaging [1–3]. At low energies, the annihilation spectra as a function of positron energy for most molecular targets are dominated by vibrational Feshbach resonances (VFRs), a process enabled by the existence of positron-molecule bound states [4,5]. These VFRs occur at incident positron energies $\epsilon_\nu = \omega_\nu - \epsilon_b$, where ω_ν is the energy of the vibrational state ν excited upon capture and ϵ_b is the binding energy. These resonances differ from true bound states in that the molecule retains sufficient energy to eject the positron by the deexcitation of a vibration. The details of this ejection process determine the positron dwell time on the molecule and, consequently, the probability of annihilation.

Intramolecular vibrational redistribution (IVR) is a process by which the vibrational energy of a molecule is redistributed into near-resonant vibrational multimode excitations [6–8]. As discussed here, this IVR process, which is central to many chemical and biological processes, plays a pivotal role in positron annihilation on molecules. The IVR coupling can occur on subpicosecond time scales [9], which can be considerably faster than the time for elastic emission of the positron due to relaxation of a fundamental, potentially allowing for coupling to many modes before positron loss occurs. Further, the emission rate from a multimode state can differ substantially from that due to VFRs involving fundamental vibrations, and thus radically alter the lifetime of a given resonance.

Previously, the importance of IVR in positron annihilation was used to explain qualitatively two specific experimental results: the dramatic increase in resonant annihilation for large alkane molecules and the reduction in resonant annihilation for these alkanes after substitution of a fluorine atom [5]. For these studies it appeared that the size of the molecule and/or the presence of a fluorine atom were the key factors as to whether IVR would be important. However, recent results for a wide variety of molecules, both large and small, have shown a broad range of similar

behavior. This necessitates a new paradigm for the understanding of the effect of IVR on positron annihilation.

Presented here are annihilation spectra and vibrational analyses for several molecules that demonstrate how IVR can enhance or suppress resonant annihilation. The focus is on specific well-isolated modes that display the effects of IVR. These analyses include the enhanced annihilation of the C=O stretch mode in acetaldehyde [10], suppression of the C-D stretch in chloroform-d, and a mix of both suppression and enhancement in chloroform (C-H and C-Cl modes, respectively). Using these results, a framework for vibrational analysis is developed that may be used to predict when IVR is expected to be important and whether it will be manifest as an enhancement or suppression of the resonance. This analysis is then used to explain the generic behavior observed in alkanes and to argue that IVR is likely important in most molecules exhibiting VFR enhanced annihilation.

Annihilation rates are expressed as the dimensionless quantity Z_{eff} , which is the measured annihilation rate λ normalized by the Dirac annihilation rate for a free-electron gas with density equal to that of the target gas [5]. The analysis here centers on comparison with the VFR model [4,5]. After subtracting a broad background, as discussed below, the data are fit to the expression

$$Z_{\text{eff}}^{(\text{fit})}(\epsilon) = \pi F \sum_{\nu} \beta_{\nu} \sqrt{\frac{\epsilon_b}{\epsilon_{\nu}}} g_{\nu} \frac{\Gamma_{\nu}^e}{\Gamma_{\nu}} f(\epsilon_{\nu} - \epsilon), \quad (1)$$

where Γ_{ν}^e is the elastic rate for ejection of a positron via the deexcitation of the fundamental vibration ν and $\Gamma_{\nu} \equiv \Gamma_{\nu}^e + \Gamma^a$ is the total loss rate, with Γ^a the annihilation rate during the time the positron is attached to the molecule. The g_{ν} are the mode degeneracies, $f(\epsilon_{\nu} - \epsilon)$ is the positron energy distribution, and $F \approx 0.66$ describes the positron-electron overlap [5]. Included in Eq. (1) are mode-scaling factors β_{ν} , which provide an empirical measure of the effects of IVR. These parameters are a measure of suppression, $\beta_{\nu} < 1$, or enhancement, $\beta_{\nu} > 1$, due to IVR. For a resonance without IVR, $\beta_{\nu} = 1$.

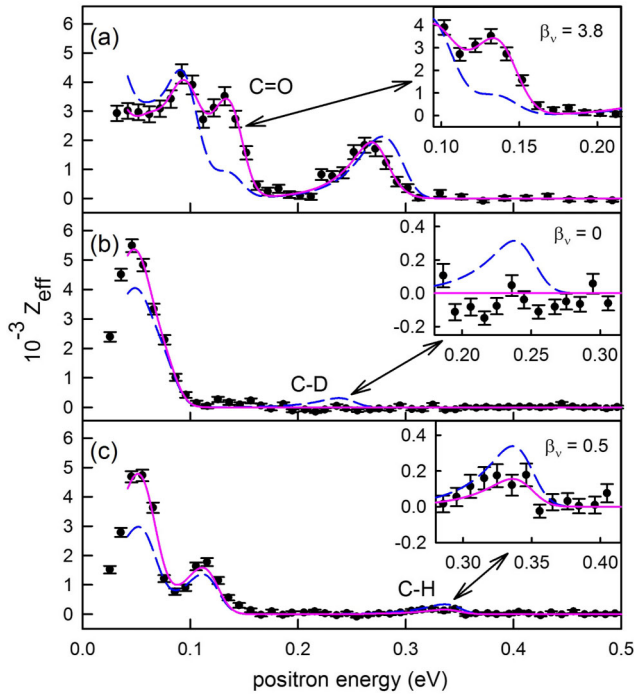


FIG. 1 (color online). Annihilation spectra for (a) acetaldehyde (C_2H_4O), (b) chloroform-d ($CDCl_3$), (c) chloroform ($CHCl_3$): (●) experimental data with the fitted SMRA and direct components subtracted off, (dashed blue line) VFR model with $\beta_\nu = 1$, (solid pink line) fitted model given by Eq. (1). Insets show the specified VFRs and fits on an expanded scale.

The magnitude of an annihilation resonance due to the excitation of a fundamental vibration is proportional to Γ_ν^e/Γ_ν . For most modes, the elastic rate is much greater than the annihilation rate, and so the ratio of $\Gamma_\nu^e/\Gamma_\nu \approx 1$. However, for weakly coupled modes, Γ_ν^e may be comparable to Γ^a , which results in a reduction in the strength of the VFR, even in the absence of IVR.

The experimental apparatus and procedures have been discussed in detail elsewhere [5]. Positrons from a ^{22}Na source are moderated in solid Ne then transferred electrostatically to a buffer gas trap. Confined radially by solenoidal magnetic fields, the positrons thermalize in the buffer gas trap to the ambient temperature through inelastic collisions with N_2 and CF_4 molecules. The cold positrons are then extracted in a pulsed beam, with a total energy spread ~ 40 meV at a pulse rate ~ 2 Hz.

Annihilation within the gas cell is monitored using a CsI crystal, which detects single annihilation gammas during a $15 \mu s$ window as a function of the cell retarding potential, yielding annihilation rates as a function of incident positron energy. As above, normalizing the annihilation rate to the Dirac rate yields the quantity Z_{eff} .

Figure 1 shows the analyzed results for the cases of acetaldehyde (C_2H_4O), chloroform-d, ($CDCl_3$), and chloroform ($CHCl_3$). The data for chloroform represent new measurements to correct systematic errors in the previous data [11]. Here we take into account the recently

discovered multimode contribution to the spectra, known as statistical multimode resonant annihilation (SMRA) [11]. The calculated SMRA curve is attenuated by a factor η , which is obtained by fitting to the data in regions between fundamental VFRs. This attenuated SMRA contribution, as well as that due to direct annihilation, has been subtracted from the data presented here to provide the clearest comparison to the VFR model. Also shown are the predictions of the VFR model with $\beta_\nu = 1$ (dashed line) and a fit with scaled VFRs (solid line).

Applying Eq. (1) and this fitting procedure to acetaldehyde and chloroform-d [Figs. 1(a) and 1(b)] yields $\eta = 0.21$ and 0.42 and $\epsilon_b = 83 \pm 1$ and 43 ± 3 meV, respectively. For chloroform [Fig. 1(c)], fitting gives $\eta = 0.35$ and $\epsilon_b = 40 \pm 1$ meV, down ~ 10 meV from the previous measurements [11]. This agrees with the study of a diverse range of other deuterated molecules and their undeuterated analogues that found that deuteration has no impact on ϵ_b , to within experimental uncertainty [12–14]. For the molecules studied here, arbitrarily varying η by 20% produces a maximum variation in ϵ_b and β_ν of 3% and 25%, respectively.

The impact of IVR on positron annihilation rates depends on three processes: mode coupling between the excited fundamental and nearby multimode states, positron ejection from the fundamental, and positron ejection from the multimode states. For simplicity, it is assumed here that the escape rate from a multimode state is dominated by the constituent mode with the largest elastic rate. For IVR to be relevant, the mode-coupling rates must be comparable to or larger than the elastic rate. Examination as to whether the excited fundamental couples to faster or slower modes will show whether to expect suppression or enhancement, respectively. Thus, knowledge of the elastic rates of the molecular vibrations, combined with an analysis of what multimode states are energetically accessible, can be used to predict qualitatively the behavior of the resonant annihilation.

The key parameters used in Eq. (1) and the analysis discussed below are listed in Tables I and II (omitting, in acetaldehyde, modes with energies above the C=O stretch). The elastic rates Γ_ν^e were calculated with experimental IR data [15,16], using Eq. (7) of Ref. [4]. It is assumed that the interaction of the incident positron with the molecule is due solely to dipole coupling, so the quoted elastic rates represent lower bounds. The tables list the modes in order of increasing energy so that they may be read as follows: all modes listed above a given mode may potentially contribute to the IVR for that mode. The results for β_ν from the fit to Eq. (1) are also listed. In cases where we cannot adequately obtain individual scale factors they have been grouped to provide an average scale factor *per mode*.

Figures 2 and 3 show a tiered model of all modes within ± 5 meV of a specific fundamental (or group of fundamentals) up to mode order 5, where the mode order

TABLE I. Mode parameters for acetaldehyde ($\epsilon_b = 83$ meV, $\Gamma^a = 0.31$ ns $^{-1}$) and chloroform-d ($\epsilon_b = 43$ meV, $\Gamma^a = 0.23$ ns $^{-1}$), including degeneracy g_ν , energy ω_ν , calculated elastic rates Γ_ν^e , and fitted IVR scale factors β_ν with the associated standard errors in parenthesis. For acetaldehyde, modes of higher energy than the C=O stretch have been left off for brevity. (\dots) indicates modes unable to eject the positron.

Mode type	ν	g_ν	ω_ν (meV)	Γ_ν^e (ns $^{-1}$)	β_ν
Acetaldehyde					
torsion	ν_{15}	1	19	\dots	\dots
C-C-O deform	ν_{10}	1	63	\dots	\dots
C-H bend	ν_{14}	1	95	0	0
CH3 rock	ν_{13}	1	107	0.18	} 0.5 (0.2)
CH3 rock	ν_9	1	114	6.3	
C-C str	ν_8	1	138	32	1.0 (0.2)
CH3 s-deform	ν_7	1	168	33	} 0.8 (0.1)
C-H bend	ν_6	1	174	27	
CH3 d-str	ν_{11}	1	176	14	
CH3 d-deform	ν_5	1	179	27	
C=O str	ν_4	1	216	380	3.8 (0.2)
Chloroform-d					
C-Cl a-deform	ν_6	2	32	\dots	\dots
C-Cl s-deform	ν_3	1	46	0.01	1.0
C-Cl s-stretch	ν_2	1	82	11	} 1.4 (0.2)
C-Cl a-stretch	ν_5	2	93	290	
C-D bend	ν_4	2	113	120	1.1 (0.3)
C-D str	ν_1	1	281	0.55	0.0 (0.1)

represents the number of fundamentals comprising the mode (i.e., fundamentals are order 1, two mode combinations are order 2, etc.). The motivation for representing the modes in this manner is that coupling to multimodes from a given initial state decreases with increasing mode order or increasing energy separation [9].

The C=O stretch mode in acetaldehyde (ν_4 at 133 meV, $\beta_\nu = 3.8$), shown in the inset of Fig. 1(a), is an example of an isolated resonance which is enhanced well above the VFR prediction. From Fig. 2(a), there are 11 multimodes near the C=O stretch, none of which contain a faster fundamental than the C=O itself ($\Gamma_\nu^e = 380$ ns $^{-1}$). In fact,

TABLE II. Mode parameters for chloroform, with $\epsilon_b = 40$ meV and $\Gamma^a = 0.22$ ns $^{-1}$. Notation is same as Table I.

Mode type	ν	g_ν	ω_ν (meV)	Γ_ν^e (ns $^{-1}$)	β_ν
Chloroform					
C-Cl a-deform	ν_6	2	32	\dots	\dots
C-Cl s-deform	ν_3	1	45	0.076	1.0
C-Cl s-stretch	ν_2	1	84	13.9	} 1.6 (0.1)
C-Cl a-stretch	ν_5	2	96	425	
C-H bend	ν_4	2	151	105	1.2 (0.1)
C-H str	ν_1	1	376	1.79	0.5 (0.1)

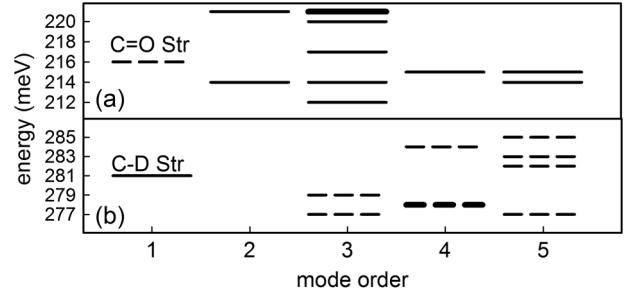


FIG. 2. Vibrational multimodes within ± 5 meV of the (a) acetaldehyde C=O stretch and (b) chloroform-d C-D stretch, up to order 5. Dashed lines are multimodes containing at least one fast escape channel. Bold lines indicate accidental degeneracies (i.e., those not due to degenerate fundamentals).

looking at Table I, the C=O stretch has a larger Γ_ν^e (i.e., shorter relaxation time) than any mode beneath it. Thus, if a positron is captured by the C=O stretch, IVR can only occur through coupling into longer-lived modes, increasing the dwell time on the molecule. The contributions of IVR are further enhanced by the relatively large 83 meV binding energy of acetaldehyde. Deexcitation of the lowest energy modes (ν_{15} and ν_{10}) does not provide enough energy to eject the positron, effectively making them dark states and further removing ejection pathways for the positron. Therefore, the enhancement of the C=O stretch VFR is a measure of the IVR to nearby multimodes.

The inset in Fig. 1(b) shows the C-D stretch mode (ν_1) in chloroform-d. Based on the binding energy, this mode should appear at 238 meV, yet is completely absent ($\beta_\nu = 0$). With $\Gamma_\nu^e = 0.55$ ns $^{-1}$, the C-D stretch is the third slowest mode in chloroform-d. Of the nine unique multimodes surrounding the C-D stretch shown in Fig. 2(b), seven contain at least one of the slower C-Cl deform modes (ν_6 and ν_3); however, *all* contain at least one quanta of the faster fundamentals (ν_2 , ν_5 , and ν_4). These modes provide open fast escape channels for the positron and suggest that, similar to the acetaldehyde C=O stretch, the consequence of IVR coupling here is one directional. Coupling from the C-D to any of the surrounding multimodes will lead to a faster ejection of the positron, thus reducing the annihilation rate.

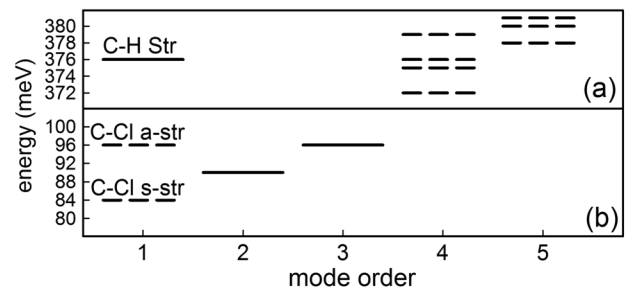


FIG. 3. Multimodes for chloroform near (a) the C-H stretch and (b) the C-Cl stretch modes. Same notation as Fig. 2.

While both enhancement and suppression appear to be present in the molecules discussed above, the C-H and C-Cl stretch modes in chloroform provide a clearer example of this competition. The vibrational parameters and mode analyses are shown in Table II and Fig. 3, respectively. The C-H stretch mode (ν_1) is the third slowest mode in chloroform. Examination of the nearby multimodes reveals that all seven contain at least one fundamental with a faster relaxation rate than that of the C-H. Thus, as before, all IVR pathways provide open escape channels, in agreement with observation ($\beta_\nu = 0.5$).

Unlike the C-H stretch, the lower energy C-Cl stretch modes (ν_2 and ν_5) can only couple into multimodes composed of the less energetic C-Cl deformations (ν_6 and ν_3). In this case IVR allows coupling only to *slower* multimodes, thus enhancing the C-Cl resonance. It is important to note that while these modes have been grouped together due to their proximity to one another, each of them individually follows this argument, and so it is expected that each will be enhanced.

For chloroform-d and chloroform, both the C-D and C-H stretch modes are suppressed by IVR; however, the amount of suppression differs considerably. Because of the shift in mode energy from deuteration, the nine multimodes near the C-D stretch are of lower order and are composed of faster escape channels. In contrast, there are only seven modes surrounding the C-H stretch in chloroform, none of which occur until fourth order. In addition, the most likely mode for the C-D stretch to couple to is the third order C-Cl a-stretch triple overtone ($3\nu_5$), which is a quadruply degenerate overtone of the fastest fundamental in the molecule. In the case of the C-H stretch, the nearest multimode is the fourth order combination $\nu_2 + \nu_3 + \nu_4 + \nu_5$, which is of higher order and has less effective escape channels. It should also be noted that IR laser studies of these molecules indicate that the IVR relaxation rate of the excited C-D stretch mode is faster than the relaxation rate of the C-H stretch mode of chloroform [17]. Thus, while both the C-D and C-H stretch modes should be suppressed due to IVR coupling, the C-D stretch is expected to be suppressed more, in agreement with the measurement.

The considerations described here provide insight into a number of previous results. The early observation of strong enhancement in the alkanes [13], and more recently in studies of molecules with strong dipole moments [14], appears to be the result of two effects. In the alkanes, 25%–50% of the fundamental vibrations are IR inactive and thus do not readily eject the positron. More importantly, for the alkanes the trend of mode elastic rates versus energy is more or less monotonic, with elastic rates increasing with mode energy. Thus, virtually all coupling between fundamentals and multimodes results in an *increase* in the lifetime of the positron-molecule complex,

and so an enhanced annihilation rate. Further, as the binding energy grows with increasing molecular size or dipole moment [14], the lowest-energy fundamentals are no longer energetically able to eject the positron (cf. the ν_6 modes of chloroform and chloroform-d), leading to a longer positron dwell time, and thus enhanced annihilation, as is observed.

Finally, fluorine substitution on the alkanes results in two effects: first, modes that were IR inactive now become active, leading to fewer dark states; second, the addition of a mode with a large elastic rate breaks the monotonic trend of the elastic rates versus energy, leading to a competition between enhancement and suppression. These two consequences of fluorine substitution yield additional escape channels for the positron, leading to a reduction in the amount of enhancement compared to the unsubstituted alkanes.

In summary, presented here are examples of small molecules that exhibit suppression and enhancement of well-isolated VFRs due to molecular IVR. It is demonstrated that vibrational analysis using a tiered model of the near-resonant multimodes can predict whether IVR will be important for a given VFR, and if so, whether it will enhance or suppress the resonance. These results show that the effects of IVR on VFRs depend strongly on the elastic rates of the fundamental vibrations. Suppression occurs when the escape rate from a multimode, accessed via IVR, is faster than escape from the fundamental vibration that the positron excited at capture. Enhancement occurs when the IVR accessed multimode contains only fundamental modes with slower escape rates than the entrance mode. Based upon these and other recent studies of small halogenated alkanes, as well as the alkanes, alcohols, and dipole-bound molecules studied previously [13,14,18], IVR appears to be nearly ubiquitous. The observation of IVR is expected whenever the near-resonant mode-coupling rates are comparable to or larger than the elastic rate of a given VFR.

A simple rate-based model of the effect of IVR on positron resonances is being developed that makes predictions in various limits [19]. While more quantitative estimates will require accurate knowledge of the mode-coupling rates, this model is intended to provide insight into the limiting behavior of VFR amplitudes, including the role of mode coupling in determining the strengths of resonances in annihilation rates. Depending upon further progress, the intimate relationship between resonant molecular annihilation spectra and mode-specific IVR could potentially provide a complementary tool to study molecular IVR processes in molecules of interest in other areas, such as chemistry and biology.

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*csurko@ucsd.edu

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