Chen, Wang, and Mazur Reply: Although the experimental technique is basically the same in both papers, there are a few experimental differences. For instance, for the excitation of the molecules we used truncated infrared pulses that have a 10-ns rise time and an ultrashort, subnanosecond fall time.[1] We did not employ longer pulses as in Ref. 2 to avoid collisional relaxation. Another difference is the wavelength of the Raman probe laser. While it is possible that either of these two facts is responsible for the reported discrepancy, the discrepancy may also be a result of the difference in data analysis and interpretation.

When the data from the Comment[3] are combined in a single logarithmic graph (see Fig. 1) with data published previously by the same authors,[2] and with the data from the Letter,[1] the spread between the author's two sets of data does not appear to be substantially smaller than the one commented upon. While the logarithmic format adopted by the authors emphasizes discrepancies at low fluence, the main argument of the Comment really hinges on discrepancies at high fluence. At a fluence of 2.1 J/cm^2, Malinovsky and Ryabov report only a single data point for each mode. In the range from 1.5 to 2.5 J/cm^2 we obtained four data points for each mode, all consistently higher.

In Ref. 2, Malinovsky and Ryabov state that "the average energy in the mode v_8 is appreciably higher than in the now reference mode v_1 over the entire range of laser fluences." This excess in energy—which in Ref. 2 is acknowledged to be in accordance with the excess observed by us—is attributed to the presence of a bimodal distribution. Since the distribution remains more or less constant over the entire fluence range, however, this explanation does not seem likely. One would expect a more gradual transition in the number of modes that are participating in the excitation process.

Malinovsky and Ryabov's conclusion of an intramolecular equilibrium without an excess of energy in the excited mode is based in part on a comparison with the results from separate calorimetric measurements. The latter were carried out with much longer, 100-ns, infrared pulses. As the authors state themselves in Ref. 2, collisional effects become important for $p\tau \geq 50$ nsTorr, with p the pressure and τ the pulse duration. Since the calorimetric measurements were carried out at a pressure of 1.35 Torr, collisional relaxation certainly occurs on the time scale of the excitation (100 ns), so it appears that the results of the calorimetric experiment may not directly be compared to the Raman-scattering results.

Finally, in their Comment,[3] Malinovsky and Ryabov point out that there is a "qualitative" disagreement because their data are "almost linear" while our data are
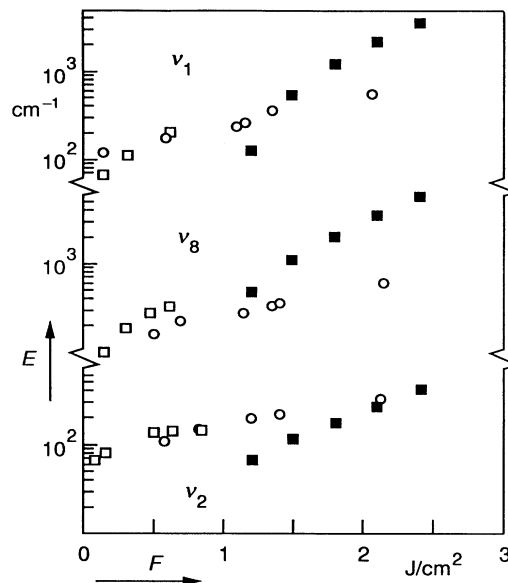

FIG. 1. Normalized Raman intensity of three modes of CF_2Cl_2 vs infrared laser fluence. The open symbols are data from the authors of the preceding Comment (circles: Ref. 3; squares: Ref. 2); the closed symbols are our own data as previously published (Ref. 1).

almost "exponential." The lines in the figure of the Comment, however, have (logarithmic) slopes ranging from 0.8 to 1.1, and those in Ref. 2 from 0.3 to 0.9. Quite in general, it is well known that for small molecules the fluence dependence is *not* necessarily linear. Reports of a power-law dependence for the infrared multiphoton excitation of small molecules abound in the literature, and in the small range of fluences measured, one cannot really distinguish an exponential from a power-law dependence.

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[1]K.-H. Chen, J. Wang, and E. Mazur, Phys. Rev. Lett. **59**, 2728 (1987).

[2]Yu. S. Doljikov, A. A. Malinovsky, and E. A. Ryabov, Laser Chem. **8**, 81 (1988).

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Comment on "Nonthermal Intramolecular Vibrational Energy Distribution in Infrared-Multiphoton-Excited CF_2Cl_2"

The observation of a nonequilibrium intramolecular distribution under ir multiphoton (MP) excitation of CF_2Cl_2 by CO_2 laser radiation is reported in the Letter by Chen, Wang, and Mazur.[1] As revealed by time-resolved spontaneous-Raman-scattering (RS) probing of the v_1, v_2, and v_8 modes, this nonequilibrium persists at least up to 10000 cm^{-1} in these three modes, and there is a tenfold overexcitation of the resonant v_8 mode with respect to the v_2 mode.

Both this conclusion and the behavior of the dependences of the average energy in the modes $\bar{\epsilon}_i$ on excitation energy fluence Φ contradict our independent measurements[2] for CF_2Cl_2 using a similar RS probing technique. To clear up this matter we made additional measurements for conditions similar to those in Ref. 1 (CF_2Cl_2 pressure, 3 Torr; CO_2 laser line, 10P32). The experimental setup and the measurement procedure have been described in Ref. 3.

The pumping-pulse duration (TEA CO_2 laser) was 25 ns. The second harmonic of a Nd-doped yttrium-aluminum-garnet laser ($\lambda = 532$ nm) with 8-ns pulse duration and time delay $\tau_d \le 20$ ns was used for RS probing, unlike Ref. 1, where use was made of the second harmonic of a ruby laser ($\lambda = 347$ nm). In addition to $\bar{\epsilon}_i$ measured in the v_1 (1098 cm^{-1}), v_2 (667 cm^{-1}), and v_8 (923 cm^{-1}) modes, we also found the values of $\bar{\epsilon}_i$ in the v_5 (322 cm^{-1}), v_3 (454 cm^{-1}), v_7 (437 cm^{-1}), and v_9 (442 cm^{-1}) modes. The results of these measurements are given in Fig. 1 (for the v_3, v_7, and v_9 modes the sum of their energies is given). There is a quantitative and a qualitative discrepancy between our results and those from Ref. 1 (also given in Fig. 1). Our measurements yield close to linear dependences $\bar{\epsilon}_i(\Phi)$, which is typical of ir MP excitation,[4] while in Ref. 1 the growth of $\bar{\epsilon}_i$ was nearer to exponential. Moreover, there is no strong overexcitation of the resonant mode v_8, and the energy ratio in low-frequency modes complies with their specific heats.

We also measured the total absorbed energy $\bar{\epsilon}_{tot}$ by direct calorimetry. The pumping pulse was 100 ns (over 80% energy in the peak; pressure, 1.35 Torr). The dependences $\bar{\epsilon}_{tot}(\Phi)$ given in Fig. 1 is similar to the energy dependence $\bar{\epsilon}_i(\Phi)$ in any of the modes. Moreover, if we sum the values of $\bar{\epsilon}_i$ in all the modes (assuming the nonprobed modes v_4 and v_6 to be in equilibrium with the
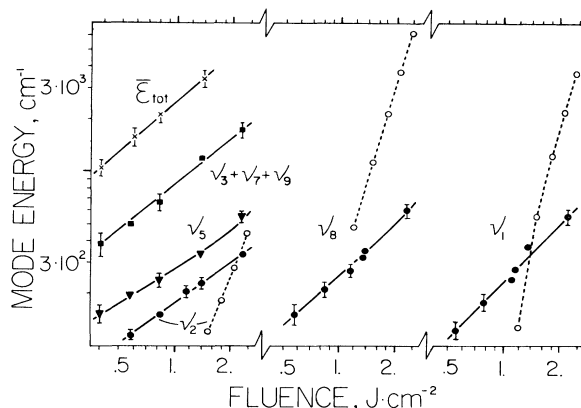

FIG. 1. Fluence dependence of the average energy in different modes of ir-MP-excited CF_2Cl_2. $\bar{\epsilon}_{tot}$ is the total absorbed energy per molecule. Open circles are the results of Ref. 1.

nonresonant ones), the result agrees well with $\bar{\epsilon}_{tot}$. All this proves that our measurements really give the true energy distribution among the various modes of CF_2Cl_2.

In conclusion, the results presented above do not confirm the existence of essential nonequilibrium for the *intramolecular* energy distribution in ir–MP-excited CF_2Cl_2 as reported in Ref. 1. Our results are consistent with the typical two-hump intermolecular distribution[3,4] when in the upper ensemble of molecules all the modes are statistically excited and in the lower one, a certain excess of energy may exist in the resonant mode(s).

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